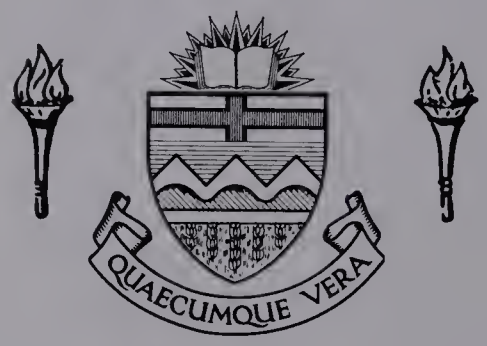

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APPLICATION OF THE PARAMETER-PERTURBATION TECHNIQUE TO THE SOLUTION OF THE MATHEMATICAL MODEL OF A CATALYST PARTICLE

BY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled APPLICATION OF THE PARAMETER-PERTURBATION TECHNIQUE TO THE SOLUTION OF THE MATHEMATICAL MODEL OF A CATALYST PARTICLE submitted by Gunnar Henningsen in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

Date .....Oct. 1967.....

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ABSTRACT

For simultaneous non-linear equations the convergence of all functional iterative procedures is dependent upon a good initial approximation to the desired root. In this report, the restriction on the choice of the initial approximation has been cased by the use of a technique known as Parameter-Perturbation.

Parameter-Perturbation divides each problem into a number of subsidiary problems, each of which is solved using an iterative procedure. Of the several functional iterative procedures available, Newton's method appears to be the most preferable for the systems of equations considered in this report.

The solution(s) to the finite-difference equations describing (a) a first-order reaction with heat effects and (b) a Langmuir-Hinshelwood type of rate mechanism, taking place in a spherical catalyst were found to agree with the published results when a sufficiently large number of grid points were employed. Due to the nature of the equations describing the Langmuir-Hinshelwood rate mechanism, convergence took more computation time than that used by the first-order reaction.

Besides the overall effectiveness factor, the solutions also give concentration(s), temperatures and local effectiveness factors as a function of radii and boundary conditions.

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I INTRODUCTION

Many chemical engineering problems give rise to non-linear simultaneous algebraic or transcendental equations. In the past a straight forcing procedure or Newton's method, Appendix Ai, have been used to obtain solutions to these sets of equations. It has been found that these methods have only limited applicability, because they depend upon a good initial estimate to the desired root(s), an estimate which is usually not available. For real systems with real solutions, the size of the domain of convergence is inversely related to the degree and number of equations.

To increase the domain of convergence, Freudenstein and Roth (1) have suggested an algorithm known as Parameter-Perturbation. This algorithm essentially consists of using a set of 'derived' equations which are similar in form to the equations to be solved. These 'derived' equations have a number of arbitrarily chosen coefficients, which may be 'perturbed', so that they can be solved by a standard iterative procedure. The 'derived' equations are then linearly deformed into the 'true' equations in a finite number of steps.

The main purpose of this report is to show how Parameter-Perturbation can be used to solve the large systems of simultaneous non-linear equations associated with the

mathematical model of a catalyst particle. The mathematical model involves dividing the catalyst's radii into N segments, with each segment assumed to have constant physical parameters. Non-linear terms arise due to the type of reaction rate equations employed in the mathematical model. Specifically considered in this report are a number of rate expressions, which are functions of both temperature and concentration. The technique employed to solve the mathematical model involves replacing the non-linear mass and energy differential equations with third-order correct finite-difference equations, Appendix Aii. Solution of these finite-difference equations makes use of the Parameter-Perturbation technique.

II PARAMETER-PERTURBATION

There is no established method for solving sets of simultaneous non-linear algebraic equations. In many cases, however, the type of solution will be known from physical considerations and iterative methods can be used. Whatever method is used to obtain a first approximation, successive corrections are usually obtained from linear equations. If the equations to be solved may be written as:

$$\underline{F}(x) = \underline{X} - \underline{f}(\underline{X}) = \underline{0}$$

or

$$\underline{X} = \underline{f}(X)$$

then the simplest iterative technique is given by the recursive formula:

$$\underline{X}^{(n-1)} = \underline{f}(\underline{X}^{(n)})$$

where the superscript designates the appropriate iterate. This particular technique exhibits geometric or first-order convergence.

Another common iterative technique is application of Newton's method to function space and is given by:

$$\underline{X}^{(n-1)} = \underline{X}^{(n)} - (\underline{J}^{-1})^{(n)} \underline{F}(\underline{X}^{(n)})$$

where $\underline{J}$ is the Jacobian matrix of partial derivatives. This method exhibits quadratic convergence, and when it does converge, does so faster than the previous method.

To solve a set of non-linear algebraic equations, assume an initial trial vector $\underline{X}^{(o)}$. Then using Newton's method obtain $\underline{X}^{(n)}$ where $\underline{X}^{(n-1)} = \underline{X}^{(n)} \pm$ specified tolerance, in n finite steps, $\underline{X}^{(n)}$ is the 'true' solution vector. However,

if the difference between corresponding elements of $\underline{X}^{(j)}$ and $\underline{X}^{(j-1)}$ becomes larger as the number of iterations increase then Newton's will not yield a solution. In this case consider the algorithm, Parameter-Perturbation.

The Parameter-Perturbation procedure is an algorithm for determining a root of a set of simultaneous non-linear equations. It is a method essentially independent of the need of a good initial approximation.

To determine a solution of a set of equations $F_i(\underline{X}) = 0$, $i=1,2,3,\ldots,n$ where $\underline{X}$ is an n-dimensional vector with components $x_1, x_2, \ldots, x_n$ and $F_i(\underline{X})$ is of the form

$$F_i(\underline{X}) = \sum_{k=o}^{m_i} P_{ik} \Phi_{ik}(\underline{X})$$

where the P_{ik} are parameters, first consider another set of equations the 'derived' equations $G_i^{(o)}(\underline{X}) = 0$, $i=1,2,\ldots,n$.

These 'derived' equations may be any set, with one known root, which belongs to the same family as $F_i(\underline{X})$, that is,

$$G_i^{(o)}(\underline{X}) = \sum_{k=o}^{m_i} Q_{ik}{}^{(o)} \Phi_{ik}(\underline{X})$$

where $Q_{ik}{}^{(o)} = P_{ik}$, except for $i=k$.

The 'derived' equations, $G_i{}^{(o)}(\underline{X}) = 0$, are deformed into the equations $F_i(\underline{X}) = 0$ by means of a finite number, N, of

successive small increments in the parameters. Define N sets of equations

$$G_i^{(j)}(\underline{X}) = \sum_{k=o}^{m_i} Q_{ik}^{(j)} \Phi_{ik}(\underline{X}) \quad , \quad j=1,2,\ldots,N$$

such that

$$G_i^{(N)}(\underline{X}) = F_i(\underline{X}) \quad ,$$

$$Q_{ik}^{(j)} = Q_{ik}^{(o)} + (P_{ik} - Q_{ik}^{(o)})\frac{j}{N}$$

The method does not require the steps to be of equal size. The desired root is obtained by solving the N sets of equations using Newton's method. The algorithm converges to a root of $F_i(\underline{X}) = 0$ if the functions $F_i(\underline{X})$ and $G_i^{(o)}(\underline{X})$ are such that:

(1) $G_i(t,x)=0$ is continuous for $0 \leq t \leq N$

(2) $\underline{X}_f(t)$ is continuous for $0 \leq t \leq N$.

To decrease the computation time it is important to choose the maximum increment for which Newton's method will converge. If upon choice of an increment size no convergence occurs, the increment is halved for the next trial. If convergence occurs for two successive trials, then for the next trial increment is doubled. An example of this procedure is given in Table 1, page 7.

An example problem is worked out in Appendix B, using Parameter-Perturbation with Newton's method. The results show that:

(1) Newton's method converges faster than the function iteration procedure.

(2) The solution is obtained using any physically feasible trial vector.

TABLE 1 Convergence Procedure

Trial Number	'Total' Increment	Increment Size	Comment
1	1.000	1.000	No convergence, reduce increment by one-half
2	.500	.500	No convergence, reduce increment by one-half
3	.250	.250	No convergence, reduce increment by one-half
4	.125	.125	Convergence, retain same increment
5	.250	.125	Convergence, double the increment
6	.500	.250	Convergence, double the increment
7	1.000	.500	No convergence, reduce increment by one-half
8	.750	.250	Convergence, retain same increment
9	1.000	.250	No convergence, reduce increment by one-half
10	.875	.125	Convergence, retain same increment
11	1.000	.125	Convergence, solution obtained

III MATHEMATICAL MODEL OF A CATALYST PARTICLE

Consider a catalyst pellet with radial symmetry, and let us focus our attention on a shell of thickness dr and radius r. Assume that the complicated diffusion phenomena within the porous structure obeys Fick's law which assumes that the diffusivity coefficient is constant for a given pressure, temperature, and pair of substances, and essentially independent of concentration.

Reactants are transported to and from the shell by diffusion and consumed within the differential shell by reaction. At steady-state, a mass balance for some component A is;

(3-1)

(Rate of diffusion of A inward at r=r+dr) - (Rate of diffusion of A inward at r=r) + (Generation of A due to reaction in the shell) = 0

In differential form this becomes;

(3-2)

$$4\pi(r+dr)^2 D_r\left(\frac{dC_A}{dr}+\frac{d^2C_A}{dr^2}dr\right)-4\pi r^2 D_r\frac{dC_A}{dr}-4\pi r^2 dr S_v f_1(C_A,C_B,..,T)=0$$

where $4\pi r^2$ is the inner superficial area of the spherical shell, D_r is the diffusivity, $\frac{dC_A}{dr}$ is the concentration gradient at the shell surface, and S_v is the pore surface, (cm^2/cm^3 of the volume of the porous structure).

(9)

The above equation (3-2) reduces to;

(3-3)

$$\frac{d^2C_A}{dr^2} + \frac{2}{r}\frac{dC_A}{dr} = \frac{f_A(C_A,C_B,\ldots,T)}{D_r}$$

(3-4)

where $S_v f_1(C_A,C_B,\ldots,T) = f_A(C_A,C_B,\ldots,T)$

A mass balance on component (i), thus yields;

(3-5)

$$\frac{d^2C_i}{dr^2} + \frac{2}{r}\frac{dC_i}{dr} = \frac{f_i(C_A,C_B,\ldots,T)}{D_r}$$

Consider the same catalyst pellet as that used in deriving equation (3-5) and assume heat transfer by conduction within the shell obeys Fourier's law, which assumes that thermal conductivity k is a function of the molecular state of the medium.

Heat is either consumed or produced within the shell due to the chemical reaction(s), and transported to or from the shell by conduction. At steady-state an energy balance on the shell becomes;

(3-6)

(Rate of conduction inward at r=r+dr) - (Rate of conduction inward at r=r) - (Rate of heat generation in shell) = 0

In differential form equation (3-6) becomes;

(3-7)

$$4\pi(r+dr)^2K\left(\frac{dT}{dr} + \frac{d^2T}{dr^2}dr\right) - 4\pi r^2K\frac{dT}{dr} - 4\pi r^2 dr\sum_i H_i f_i(C_A,C_B,..,T)=0$$

where K is the effective thermal conductivity coefficient, $\frac{dT}{dr}$ is the thermal gradient at the shell surface.

The above equation (3-7) reduces to;

(3-8)

$$\frac{d^2T}{dr^2} + \frac{2}{r}\frac{dT}{dr} = \sum_i \frac{H_i f_i(C_A, C_B, \ldots, T)}{K}$$

Reasoning similar to that used in obtaining equations (3-5) and (3-8) for a spherical shell, enables one to derive the corresponding equations for cylindrical and slab geometry.

For cylindrical geometry the equations are;

(3-9)

$$\frac{d^2C_i}{dr^2} + \frac{1}{r}\frac{dC_i}{dr} = \frac{f_i(C_A, C_B, \ldots, T)}{D_r}$$

and (3-10)

$$\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} = \sum_i \frac{H_i f_i(C_A, C_B, \ldots, T)}{K}$$

where i refers to components A, B, ...

For a one-dimensional slab the equations are;

(3-11)

$$\frac{d^2C_i}{dx^2} = \frac{f_i(C_A, C_B, \ldots, T)}{D_x}$$

and

(3-12)

$$\frac{d^2T}{dx^2} = \sum_i \frac{H_i f_i(C_A, C_B, \ldots, T)}{K}$$

These equations have the following boundary conditions;

(3-13)

At r = R

$$C_i = C_{is}$$

$$T = T_s$$

At x = L

$$C_i = C_{is}$$

$$T = T_s$$

(3-14)

At r = 0

$$\frac{dC_i}{dr} = 0$$

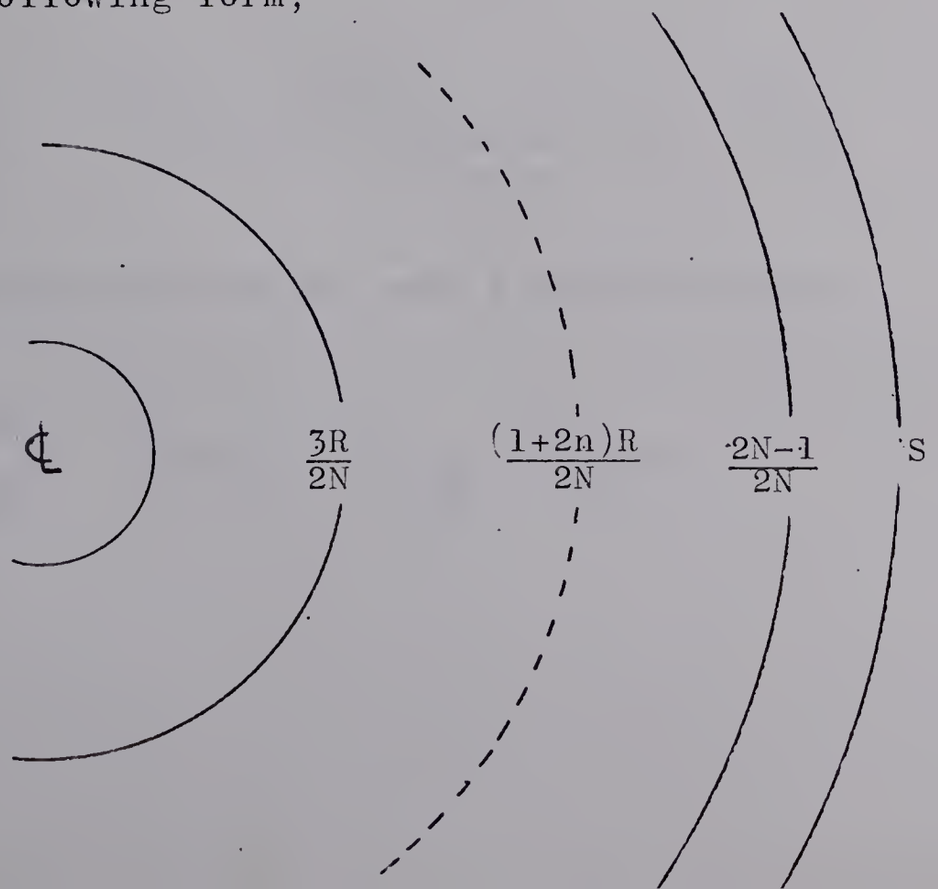
$$\frac{dT}{dr} = 0$$

At x = 0

$$\frac{dC_i}{dx} = 0$$

$$\frac{dT}{dx} = 0$$

The grid system employed for a spherical catalyst is of the following form;



where N is the total number of grid points

n position of grid points, calculated from the centre.

The finite-difference approximation for the space derivatives are:

(3-15)

$$\frac{d^2T}{dr^2} = \frac{T_{n+1} - 2\,T_n + T_{n-1}}{\Delta r^2} \qquad n = 1,2,\ldots,N-1$$

(3-16)

$$\frac{dT}{dr} = \frac{2\,T_{n+1} + 3\,T_n - 6\,T_{n-1} + T_{n-2}}{6\Delta r} \qquad n = 1,2,\ldots,N-1$$

for n=N, outermost grid point, the space derivative are;

(3-17)

$$\frac{d^2T}{dr^2} = \frac{-T_{N-2} + 10\,T_{N-1} - 25\,T_N + 16\,T_S}{5\Delta r^2}$$

(3-18)

$$\frac{dT}{dr} = \frac{3\,T_{N-2} - 20\,T_{N-1} - 15\,T_N + 32\,T_S}{30\Delta r}$$

Similarily for the mass balance we have;

(3-19)

$$\frac{d^2C_i}{dr^2} = \frac{C_{i,n+1} - 2\,C_{i,n} + C_{i,n-1}}{\Delta r^2}$$

(3-20)

$$\frac{dC_i}{dr} = \frac{2\,C_{i,n+1} + 3\,C_{i,n} - 6\,C_{i,n-1} + C_{i,n-2}}{6\Delta r}$$

(3-21)

$$\frac{d^2C_i}{dr^2} = \frac{-\,C_{i,N-2} + 10\,C_{i,N-1} - 25\,C_{i,N} + 16\,C_{i,S}}{5\Delta r^2}$$

(3-22)

$$\frac{dC_i}{dr} = \frac{3\,C_{i,N-2} - 20\,C_{i,N-1} - 15\,C_{i,N} + 32\,C_{i,S}}{30\Delta r}$$

where n = 1,2,...,N-1

i = components of the system

Once the set of finite-difference equations, approximating the mathematical model's differential mass and energy balances, have been solved for the concentration and temperatures, it is possible to obtain the local and overall effectiveness factors for the catalyst particle.

The local effectiveness factor η_L, is defined as;

(3-23)

$$\frac{\text{Rate of reaction at } r = r}{\text{Rate of reaction at } r = R} \quad \text{or} \quad \frac{f_i(C_A, C_B, \ldots, T)}{f_i(C_{As}, C_{Bs}, \ldots, T_S)}$$

The overall effectiveness factor η, is defined as;

$$\frac{3\int_0^R r^2 f_i(C_A, C_B, \ldots, T)\, dr}{R^3 f_i(C_{As}, C_{Bs}, \ldots, T_S)} \qquad (3\text{-}24)$$

It was decided to integrate equation (3-24) piecewise, fitting exactly through the points a fourth degree polynomial to each segment. The derivation is given in Appendix Aiii.

The rate constant(s) are considered to be a function of the absolute temperature and the activation energy associated with the reaction, i.e.

$$k_v = k_{vs} e^{\left(\frac{E}{R_g T_s} - \frac{E}{R_g T}\right)} \qquad (3\text{-}25)$$

The derivation of equation (3-25) is given in Appendix Aiv.

IV DETAILS OF SOLUTION

(a) First Order Irreversible Reaction With Heat Effects

To show the applicability of Parameter-Perturbation in finding the solution to systems of simultaneous non-linear equations we have chosen as our first system a mathematical model describing an irreversible, first order reaction with heat generation. The equations describing this first order reaction are as follows:

Stoichiometry (4-1)

$$X \longrightarrow \text{Products}$$

Rate (4-2)

$$r_x = k_{vs} e^{\left(\frac{E}{R_g T_s} - \frac{E}{R_g T} \right)} \cdot C_x$$

The solutions to the mathematical model of an irreversible first order reaction with heat generation have been presented by a number of people, some of whom are; Weisz and HIcks (3), Tinkler and Metzner (4), and Carberry (5). However none of the solutions presented up to now have made any use of the finite-difference technique employed in this report. In order to present the solution in a standard form it is necessary to define the following dimensionless parameters:

(4-3)

$$\Phi = \frac{R^2 k_{vs}}{D_r} \eta$$

(4-4)

$$\gamma = \frac{E}{R_g T_s}$$

(4-5)

$$\beta = - \frac{C_{xs} H D_r}{T_s K}$$

Employing the mathematical model presented in Section III with the specific modifications as given by equations (4-1) to (4-5) inclusive the Parameter-Perturbation algorithm was used to obtain temperatures and concentrations in the catalyst particle as a function of the dimensionless parameters γ, Φ and β.

The solutions to the mathematical model describing an irreversible first order reaction are presented as η versus γ, Φ and β. Figure 1, page 18 shows the graphical representation of these results for $\gamma = 30$, $\beta = 0.0$, .05 and -.20, also shown are the corresponding values obtained by Weisz and Hicks. Numerical results are compared in Table 2, page 34.

Using limited numerical accuracy, core storage limited to 70,000, it was observed that no numerical convergence could be obtained for cases where $\gamma \cdot \beta > +.15$. No problems

of convergence were encountered with endothermic first order reactions. Refer to Table 3, page 37.

With the transformation used by Weisz and Hicks only the overall effectiveness factor can be obtained,but with the finite-difference approach concentration,temperature and effectiveness factor as a function of the reduced radii can be solved for.Example plots of reduced concentration, effectiveness factor and temperature versus reduced radii are given in Figures 2, 3 and 4 respectively. A more complete tabulation of results is available from the Chemical Engineering Department. Figures 2 , 3 and 4 show that the major change in concentration and temperature takes place in the outer one-third of the spherical catalyst.

FIGURE 1

Comparison of Effectiveness Factors in Terms of Observable Parameters

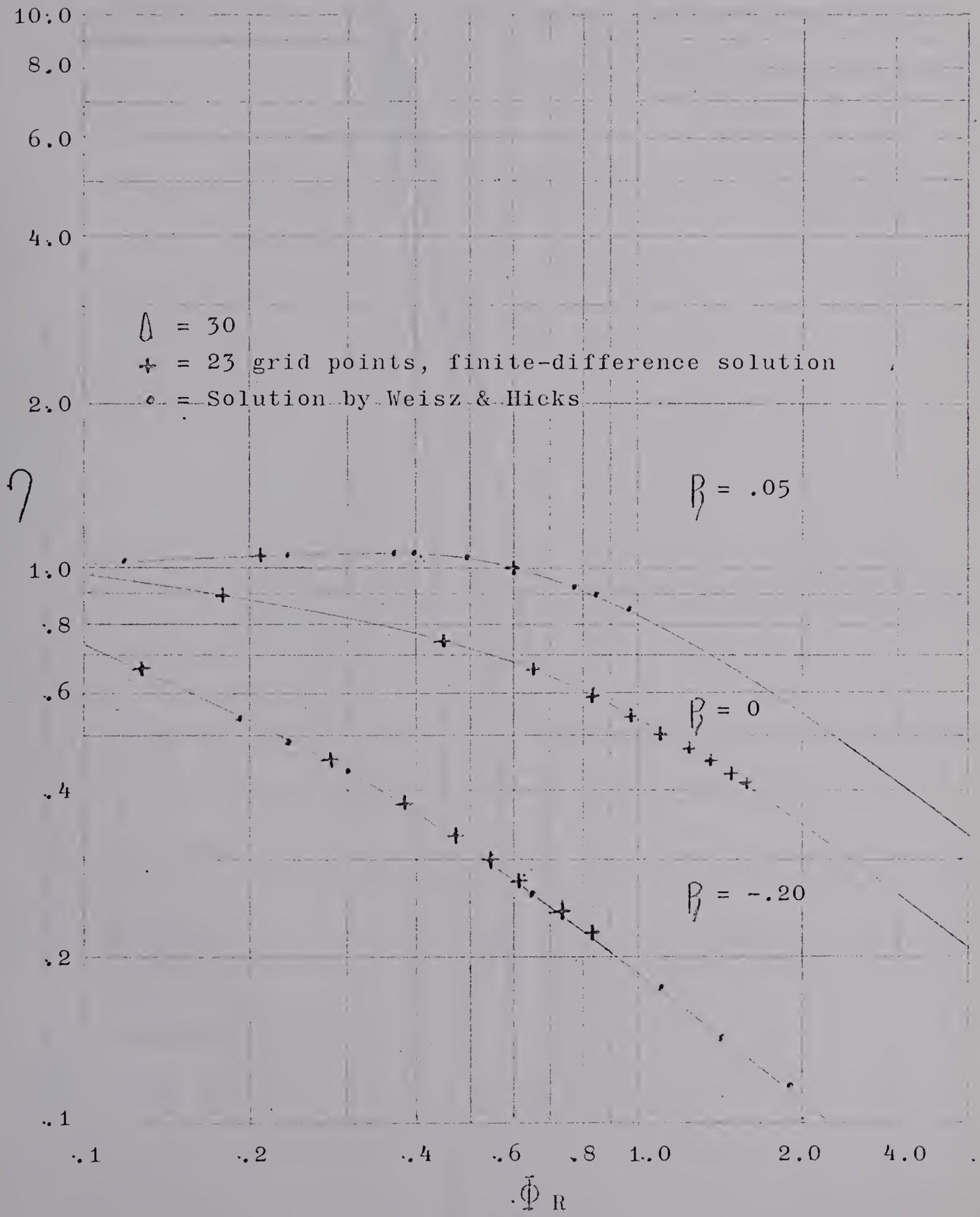


FIGURE 2

Reduced Concentration versus Reduced Radii, First Order

(1) $\Phi = 2.108$, $\beta = 0.05$

(2) $\Phi = 1.778$, $\beta = 0.00$

(3) $\Phi = 1.275$, $\beta = -.20$

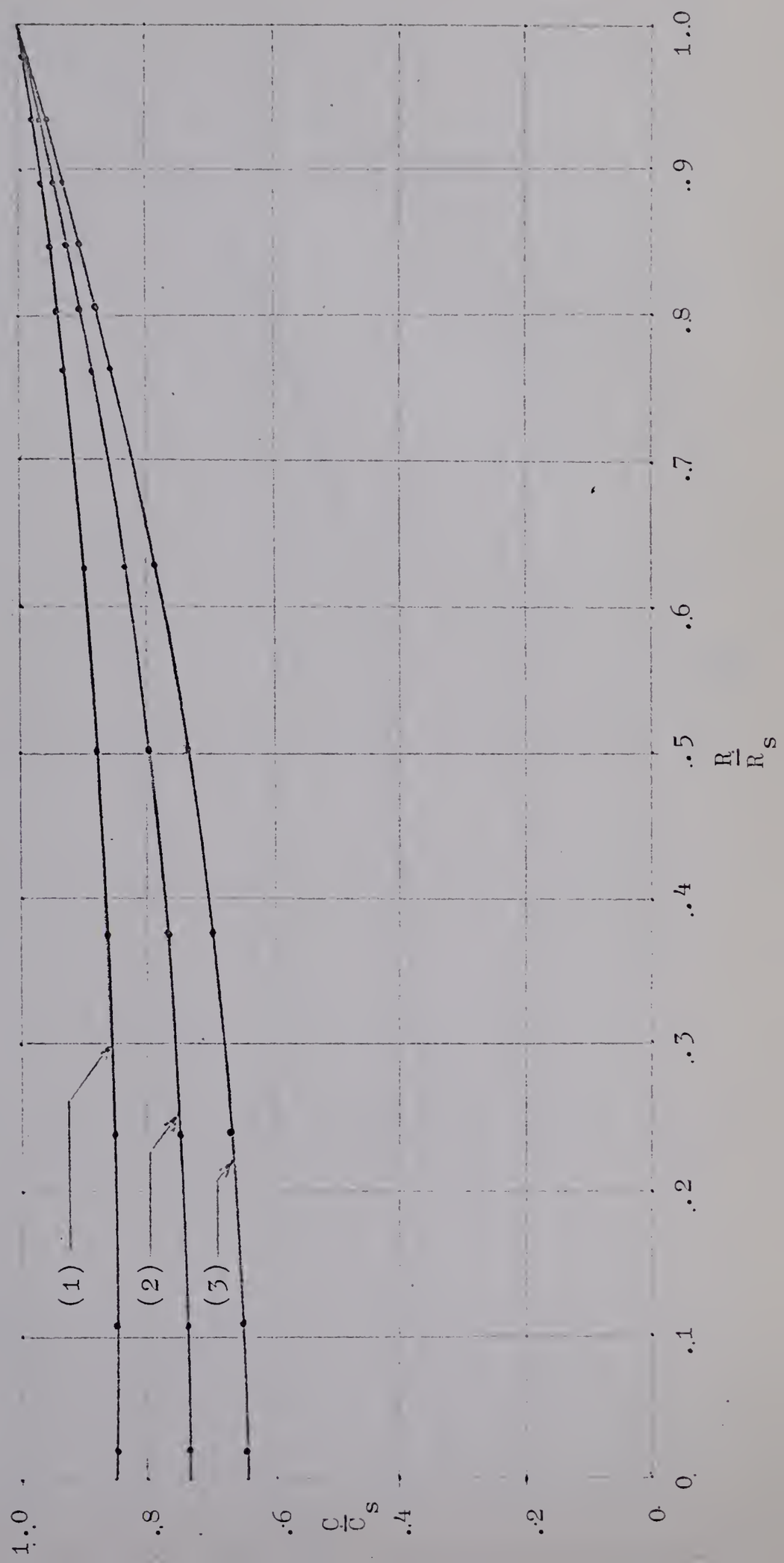
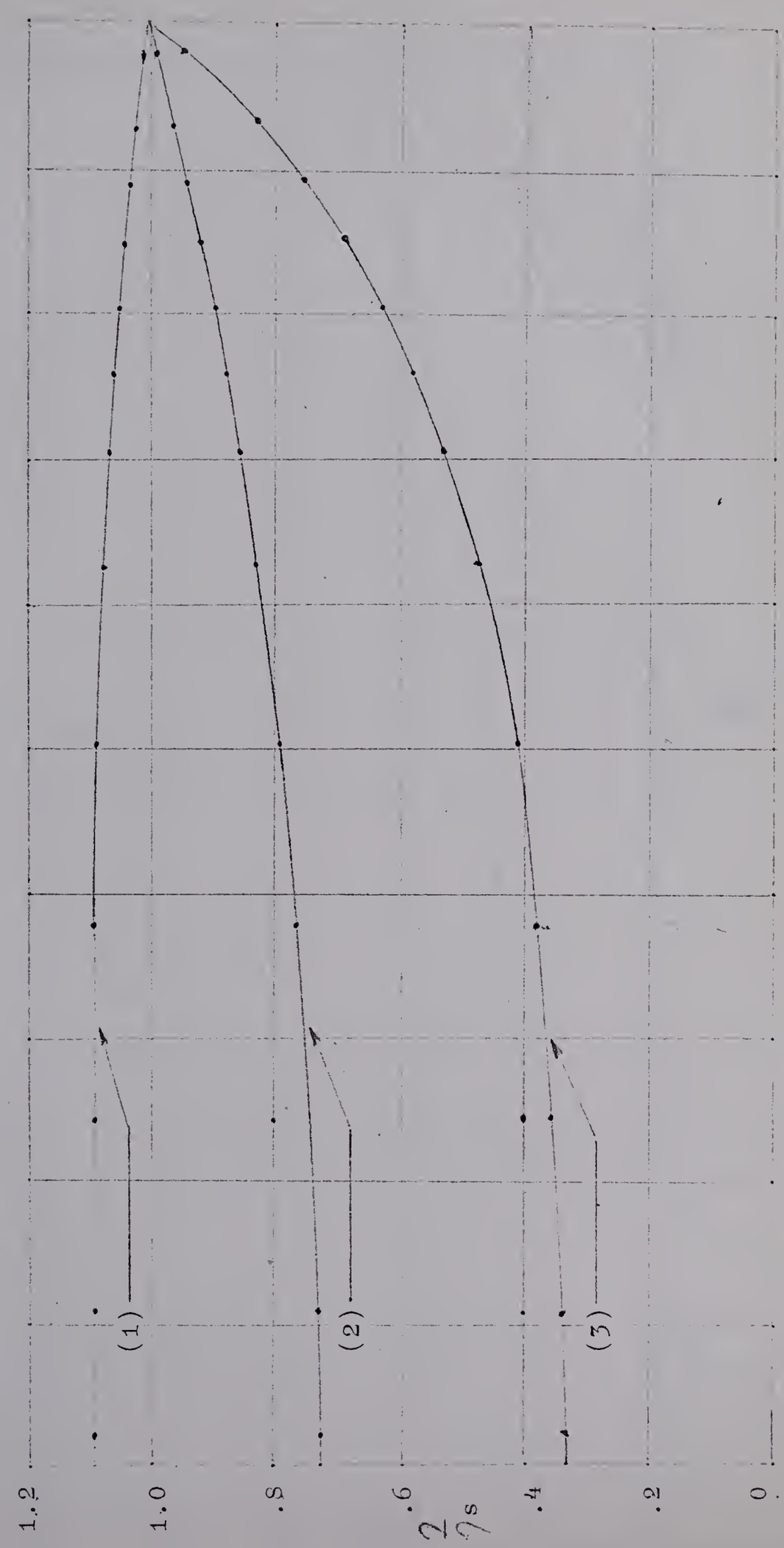


FIGURE 3

Local Effectiveness Factor versus Reduced Radii, First Order

(1) $\Phi = 2.108$, $\beta = .05$; (2) $\Phi = 1.778$, $\beta = 0$; (3) $\Phi = 1.275$, $\beta = -.20$



Reduced Temperature versus Reduced Radii, First Order

(1) Φ = 2.108, β = .05

(2) Φ = 1.275, β = -.20

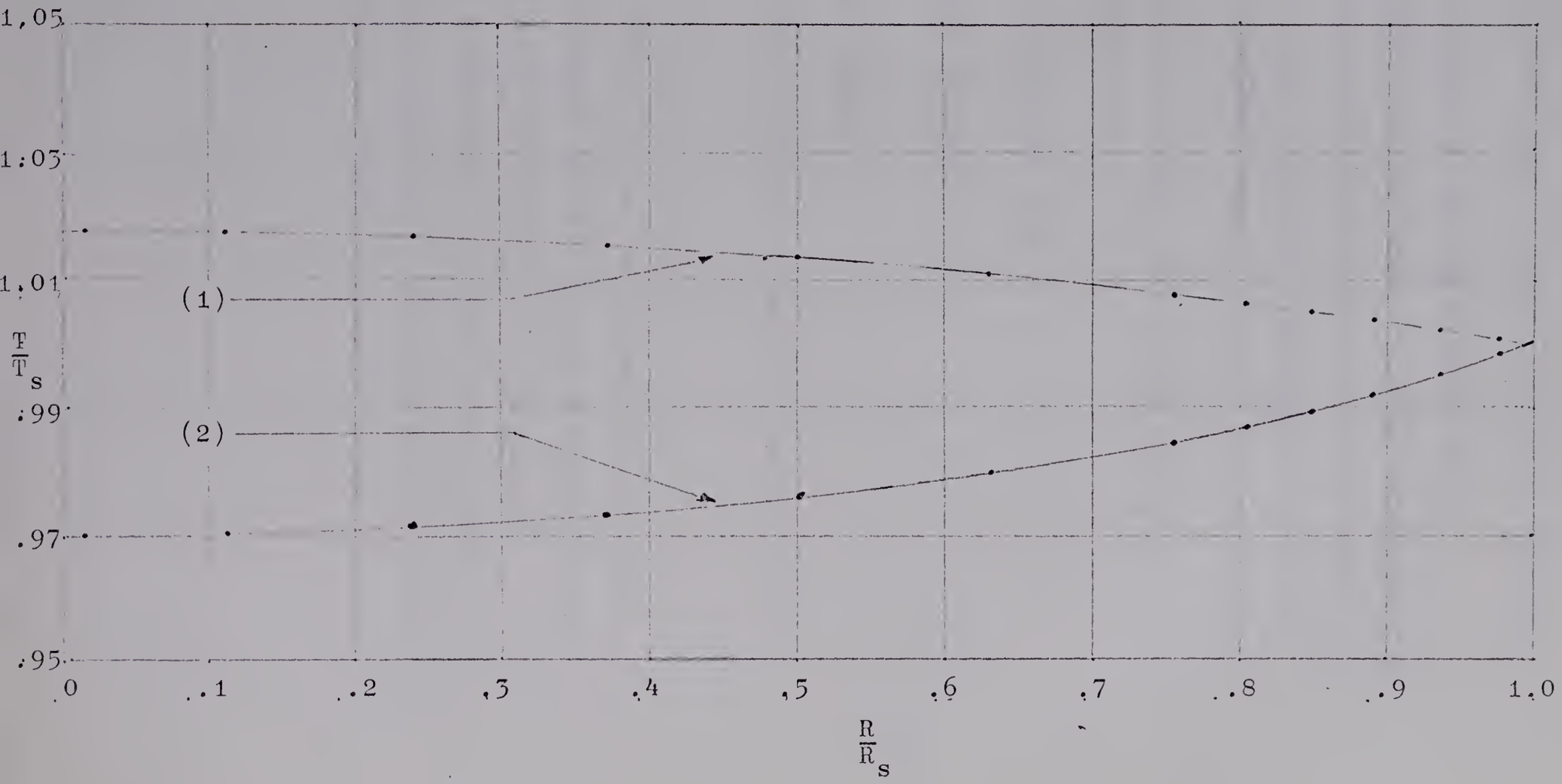


FIGURE 4

(b) Langmuir-Hinshelwood Reaction With Heat Effects

For our second example of the applicability of Parameter-Perturbation we propose to find the solution(s) to the mathematical model of a reaction taking place in a spherical catalyst, where the rate expression is of the Langmuir-Hinshelwood type.

The general chemical equation describing reactions under consideration are;

$$A + bB + \ldots + \longrightarrow xX + yY + \ldots \tag{4-6}$$

The rate equation is taken to be,

$$r = kp_A/(1+K_A p_A + \sum_i K_i p_i) \tag{4-7}$$

where i denotes any reaction product or reactant other than A.

Effectiveness factors for an isothermal catalyst have recently been presented by Roberts and Satterfield for a catalyst of slab geometry (6). Their method of solution can be summarized as follows. First assume: a slab geometry; ideal gas behaviour; an effective diffusivity for each species which is constant but not necessarily equal to each other.

A material balance on component A, over a differential thickness within the catalyst, gives

$$D_A \frac{d^2C}{dx^2} = D_A \left(\frac{1}{RT}\right) \frac{d^2P_A}{dx^2} = r \qquad (4\text{-}8)$$

A similar balance on any other species gives

$$D_i \left(\frac{1}{RT}\right) \frac{d^2P_i}{dx^2} = -\nu_i r \qquad (4\text{-}9)$$

where ν is the stoichiometric coefficient.

Combine equations (4-8) and (4-9) and integrate subject to the boundary conditions $p_A = p_{A,s}$; $p_i = p_{i,s}$ at $x=0$ and

$$\frac{dP_A}{dx} = \frac{dp_i}{dx} = 0 \quad \text{at } x = L \qquad (4\text{-}10)$$

to yield an expression for p_i in terms of p_A.

Substistuting the resulting expression into equation (4-7) gives

$$r = \frac{kp_A}{(1+p_A(K_A - D_A \sum_i (K_i \nu_i / D_i)) + \sum_i K_i (p_{i,s} + (p_{A,s} \nu_i D_A / D_i)))} \qquad (4\text{-}11)$$

Define $$w = 1 + \sum_i K_i (p_{i,s} + (p_{A,s} \nu_i D_A / D_i)) \qquad (4\text{-}12)$$

Note: Only positive values of w can be handled.

(4-13)

Define $k' = k/w$

and

(4-14)

$$K_o = (K_A - D_A \sum_i (K_i \gamma_i / D_i))/w$$

Using these definitions, equation (4-11) reduces to

(4-15)

$$r = k' p_A / (1 + K_o p_A)$$

Equation (4-15) may be substistuted into equation (4-8) and integrated to give

(4-16)

$$\frac{d(K_o p_A)}{d(x/L)} = -\sqrt{2}\,\phi_M \left(K_o (p_A - p_{A,o}) - \ln\left(\frac{1+K_o p_A}{1+K_o p_{A,o}}\right)\right)^{\frac{1}{2}}$$

where $\phi_M = L \left(\frac{k' R T}{D_A}\right)^{\frac{1}{2}}$

In terms of present nomenclature the effectiveness factor is then defined as

(4-17)

$$\eta = \frac{\sqrt{2}}{\phi_M} \left(\frac{1+K_o p_{A,s}}{K_o p_{A,s}}\right) \left(K_o (p_{A,s} - p_{A,o}) - \ln\left(\frac{1+K_o p_{A,s}}{1+K_o p_{A,o}}\right)\right)^{\frac{1}{2}}$$

where $p_{A,o}$ is determined by numerically integrating equation (4-16)

where

$p_{A,o}$ is the partial pressure at the center of the catalyst particle

K_o overall adsorption constant

k rate constant

k' modified rate constant

$p_{A,s}$ partial pressure at the surface

Employing the mathematical model as defined in Section III, which differs from that used by Roberts and Satterfield because the former is for a spherical catalyst pellet with heat generation. For spherical coordinates the solution is as follows;

Mass balance

(4-18)

$$\frac{D_r}{R_g T}\left(\frac{d^2 p_A}{dr^2} + \frac{2}{r}\frac{dp_A}{dr}\right) = \frac{k' p_A}{1+K_o p_A}$$

Similarily the energy balance is

(4-19)

$$K\left(\frac{d^2 T}{dr^2} + \frac{2}{r}\frac{dT}{dr}\right) = \frac{\Delta H_i k' p_A}{1+K_o p_A}$$

where $k' = \left(\frac{k}{w}\right) e^{\left(\frac{E}{R_g T_s} - \frac{E}{R_g T}\right)}$

Solutions using Parameter-perturbation were obtained for the system C, CO_2 previously investigated by Austin and Walker (7). However K_o was held constant for the solutions obtained, the error introduced by this simplification is not known.

Results of η versus Φ, β and $p_{As}K_o$, obtained by using

Parameter-Perturbation to solve the sets of finite-difference equations representing both spherical and slab geometry are presented for the system carbon, carbon-dioxide in Figure 5 page 28 .

The approach employed by Roberts and Satterfield applies only to slab geometry, and for reactions without any heat generation. As noted from equation (4-9) only the overall effectiveness factor can be evaluated. However with the finite-difference approach any type of geometry can be used, as well as reactions with heat generation. Concentration, effectiveness factor and temperature are solved for as functions of the reduced radii.

Example plots of reduced concentration, effectiveness factor and temperature versus reduced radii are given in Figures 6, 7 and 8 pages 29 ,30 and 31 respectively, for $p_{As}K_o = -.964$. A more detailed tabulation of results are available from the Chemical Engineering Department.

From the calculations carried out using both spherical and slab geometry for $p_{As}K_o = -.964$ it was observed that:

(a) Effect of heat generation on overall effectiveness factor is neglible for a surface temperature of 1273^oK, assuming K_o to be constant.

(b) The effectiveness factors calculated for $p_{As}K_o = -.964$ are much lower than the corresponding effectiveness factors for a first order reaction with identical physical parameters.

(c) Plots of overall effectiveness factors as a function of the parameters Φ, β and $p_{As}K_o$ for the cases solved by both Roberts and myself coincide, but if we make use of the transformation $L^2 = R^2/9$ proposed by R. Aris (9) to convert from linear to spherical coordinates the results obtained from linear coordinates do not coincide with my results for the spherical system. Thus one is led to the conclusion that for this particular rate mechanism and $p_{As}K_o = -.964$ the transformation does not hold.

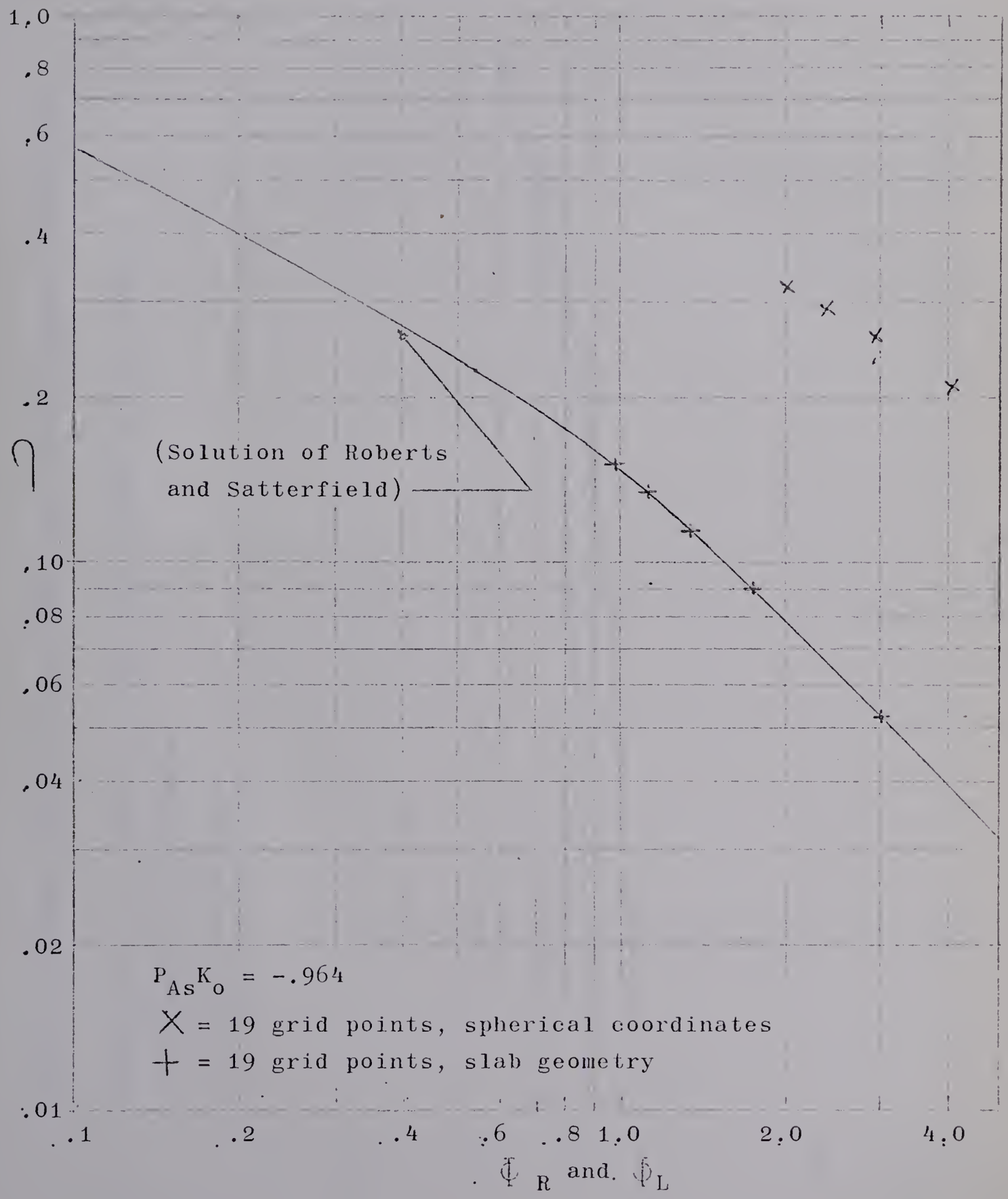
From Figures 6, 7 and 8 pages 29, 30 and 31 respectively the following is observed:

(a) Concentration, effectiveness factor and temperature gradients are steepest near the surface.

(b) Concentration near the centre of the particle is high in comparison to the corresponding effectiveness factor.

FIGURE 5

Comparison of Effectiveness Factors in Terms of Observable Parameters



Partial Pressure versus Reduced Radii and Length, Langmuir-Hinshelwood

Parameters (D = .225, α = .001, $k_{vs} = 5*10^{-7}$, P_{As} = .750)

(1) Spherical Coordinates

(2) Linear Coordinates

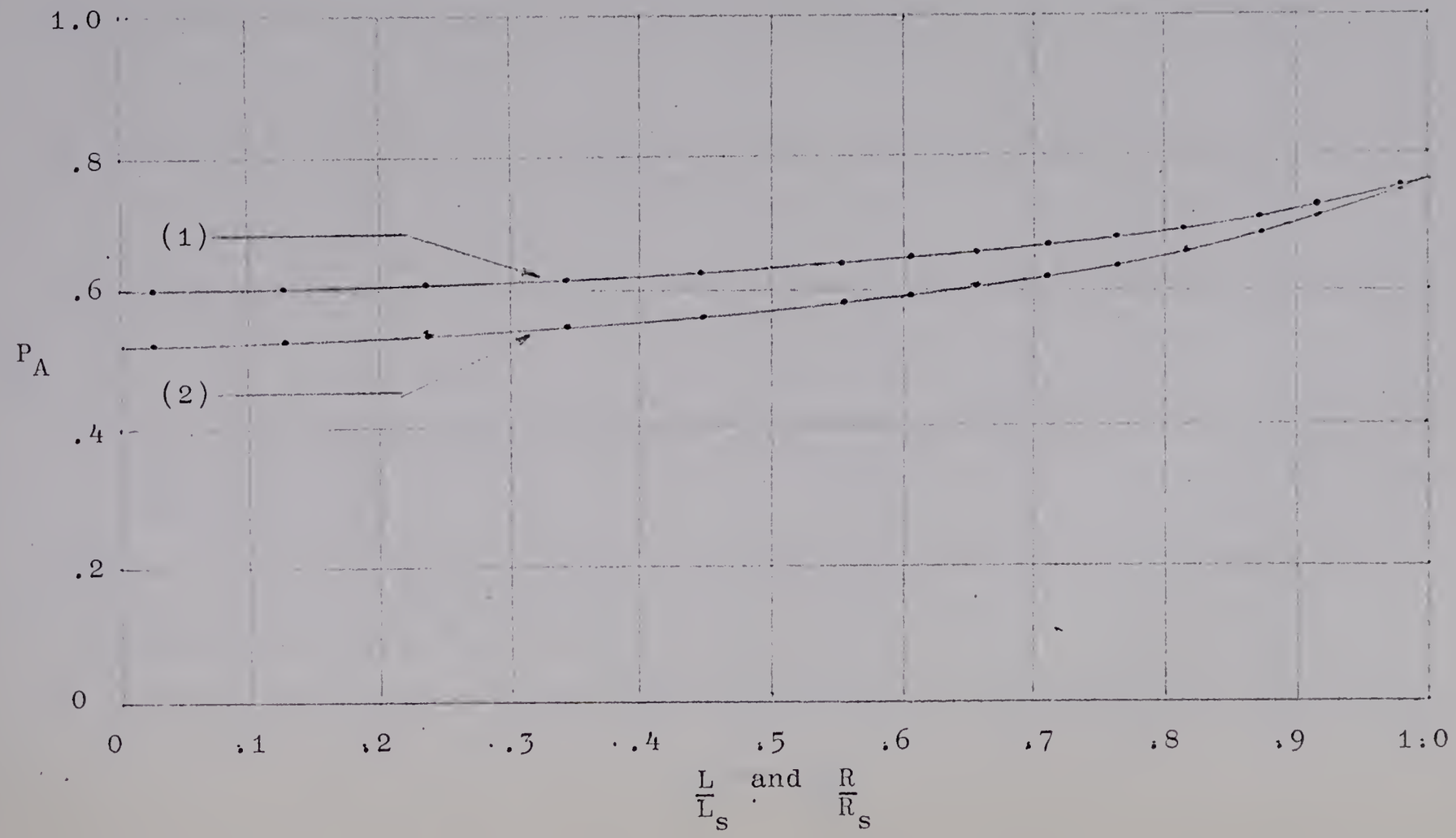


FIGURE 6

Local Effectiveness Factor versus Reduced Radii and Length, Langmuir-Hinshelwood

Parameters (D = .225, $\quad$ = .001, $k_{vs} = 5*10^{-7}$, $P_{As} = .750$)

(1) Spherical Coordinates

(2) Linear Coordinates

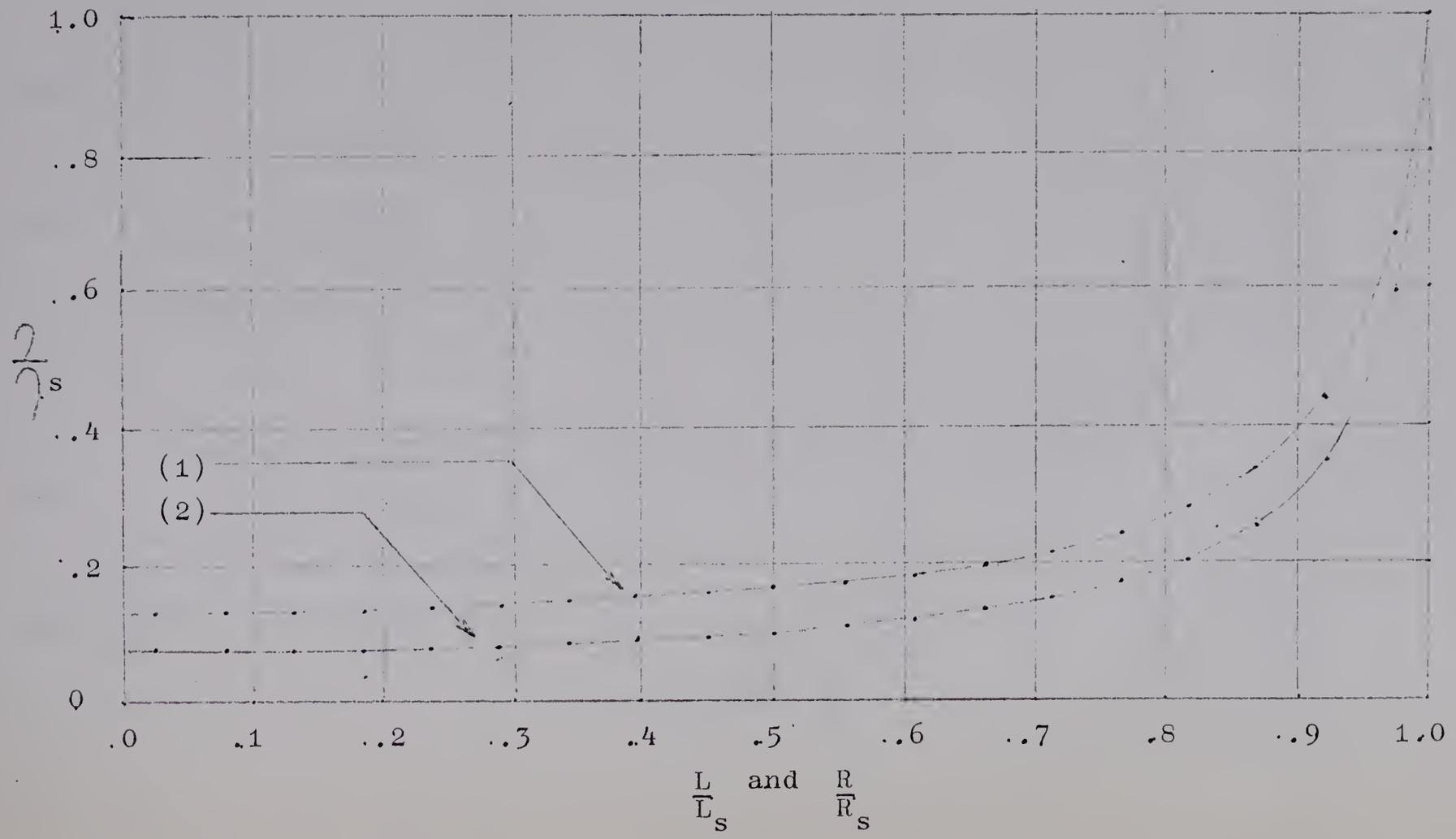


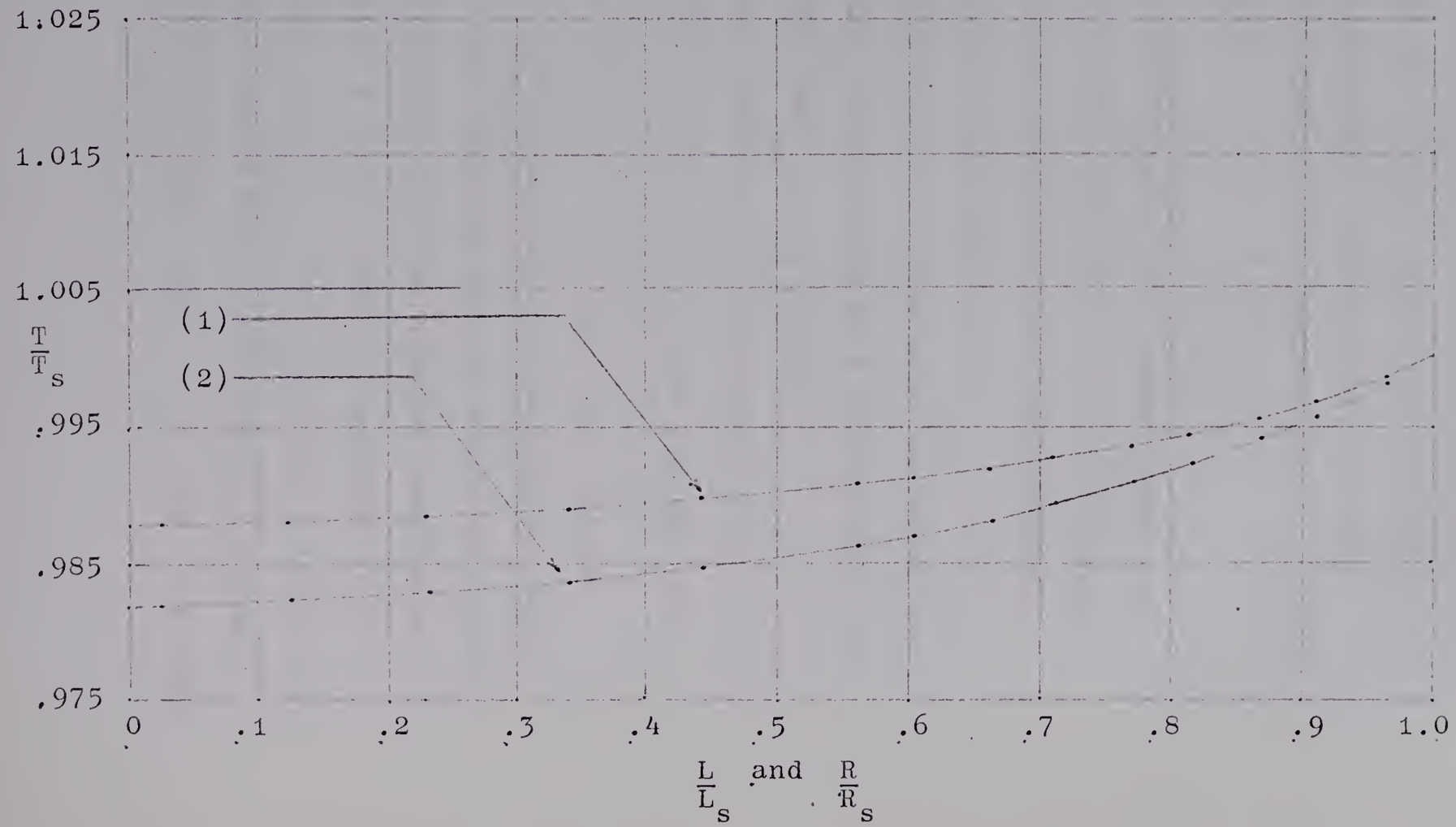
FIGURE 7

FIGURE 8

Reduced Temperature versus Reduced Radii and Length, Langmuir-Hinshelwood

Parameters (D = .225, α = .001, $k_{vs} = 5*10^{-7}$, P_{As} = .750, ΔH = 50,000)

(1) Spherical Coordinates (2) Linear Coordinates



V RESULTS

The calculation algorithm carried out by the computer program will work for a wide variety of problems and has the following features which differ from the calculation methods employed by other workers in this field of catalysis.

(1) The initial trial vector $\underline{X}^{(o)}$, describing the concentrations and temperatures in the interior of the catalyst consist of the known surface concentration(s) and temperature.

(2) Thermal conductivity and diffusion coefficients can be fed into the program as a function of the radii, if this function is known.

(3) Concentration, temperature and effectiveness factor are calculated as functions of the reduced radii.

To minimize round-off error the finite-difference equations are multiplied by arbitrary constants, such that all the equations have parameters which are of the same order of magnitude. For the systems considered in this report we chose 1 as the order of magnitude with which to work. Convergence to an acceptable solution for the individual grid system being considered is assumed whenever the residual of each equation is less than .0005.

The accuracy with which the system of finite-difference equations are solved by the computer is dependent only upon the accuracy with which the 'true' set of equations are solved, and not upon the number of 'deformed' sets of equations used to arrive at the 'true' set of equations.

Table 2 is a summary of some of the solutions obtained by the Parameter-Perturbation algorithm. These results are compared to solutions obtained by Weisz and Hicks for $\beta = -.20$ and $\beta = +.05$ and to the analytical solutions for the case where $\beta = 0$, these comparisons are all for a first order rate mechanism. To show that numerical convergence has been obtained, a comparison of center line concentrations obtained using 19 and 23 grid points, for both First Order and Langmuir-Hinshelwood rate mechanisms are shown.

TABLE 2 Error Calculations for Effectiveness Factor

Rate Mechanism	ϕ	β	$\eta^{(1)}$	$\eta^{(2)}$	%Error (3)
First Order	1.778	0.00	.889	.888	.11
(Spherical - Coordinates)	6.537	0.00	.654	.652	.31
	12.356	0.00	.475	.473	.42
	15.587	0.00	.410	.408	.50
	2.108	.05	1.054	1.054	.00
	6.005	.05	1.001	1.000	.10
	1.275	-.20	.637	.635	.31
	6.746	-.20	.259	.257	.78

Rate Mechanism	D_x	β	k_{vs}	$C_o^{(4)}$	$C_{\ell}^{(5)}$	Numerical Error (6)
First Order	.005	0.00	.010	.731	.731	0.0
(Spherical - Coordinates)	.005	0.00	.190	.026	.026	0.0
	.005	-.20	.010	.849	.849	0.0
	.005	-.20	.190	.552	.552	0.0
	.005	+.05	.010	.640	.640	0.0

Rate Mechanism	D_x	k_{vs}	$P_{As}K_o$	$P_A^{(4)}$ ¢	$P_A^{(5)}$ ¢	Numerical Error
Langmuir-Hinshelwood	.025	5×10^{-7}	-.964	.354	.354	0.0
	.225	5×10^{-7}	-.964	.602	.602	0.0
(Spherical - Coordinates)						

where:

(1) Overall effectiveness factor calculated using Parameter-Perturbation and 23 grid points.

(2) Overall effectiveness factor as calculated by Weisz and Hicks (β = -.20 and +.05) or by analytical means (β = 0.0).

(3) $$\% \text{ Error} = \frac{\text{Calculated} - \text{Published}}{\text{Published}} \times 100$$

(4) Centerline concentration calculated using 23 grid points.

(5) Centerline concentration calculated using 19 grid points.

(6) Numerical error = difference between results obtained by using 23 and 19 grid points.

From the brief error analysis, Table 2, it is obvious that the number of grid points required for a finite-difference representation of highly non-linear differential equations is high. Another source of error, aside from the finite-difference approximations, is the numerical integration procedure required to obtain an overall effectiveness factor. However, since integration is a smoothing process, errors generated are usually small.

Newton's method of convergence was found to be adequate by itself whenever only endothermic heat effects were considered. Exothermic systems however presented a much more difficult problem. Using limited numerical accuracy it was not possible to solve any problems for which $\Delta \cdot B < .15$.

Without exception numerical solutions to problems where $\beta > .15$, the residuals of the finite-difference equations could not be made to approach zero, thus making it impossible to obtain a solution, reference Table 3, page 37 . The reason for this appears to be the limited numerical accuracy of the computer, total core storage of 70,000, and not a fault of the method used. An inspection of the finite-difference matrix revealed that the non-linear term is of an order of one-hundred of the magnitude of the linear terms, thus to handle this problem requires a large computer pocessing almost unlimited numerical accuracy. This appears to be the major limit of the finite-difference approach.

The application of the Parameter-Perturbation technique to orders other than those given in this report follows the same general procedure as those solved here, reference Appendix C, this is an advantage of this method of solution over methods presented in the literature. Furthermore the method outlined in Appendix C applies to systems which have not been solved by any other approach.

Thus the Parameter-Perturbation technique with Newton's method is a general method of solution to the various proposed rate expressions. The calculation time required is of the order of 20 seconds, I.B.M. 7020, to obtain a complete solution to any particular rate expression.

TABLE 3 Summary Of Computer Output For $\Delta \cdot \beta = .18$

$\frac{C_1}{C_s}$	$\frac{C_N}{C_s}$	$\frac{T_1}{T_s}$	$\frac{T_N}{T_s}$	R_1	R_N	R_1	R_N	No. of Iteration
1.757	1.016	.824	.995	1.066	.001	.686	.000	1
1.034	.996	1.002	1.000	.323	.004	.054	.000	2
.616	.984	1.034	1.001	.015	.002	.005	.000	3
.594	.983	1.033	1.001	.000	.002	.076	.000	4
.644	.984	1.023	1.001	.006	.002	.343	.000	5
.643	.984	1.023	1.001	.001	.002	.325	.000	6
.632	.984	1.025	1.001	.006	.002	.229	.000	7
.632	.984	1.025	1.001	.006	.002	.232	.000	8
.632	.984	1.025	1.001	.006	.002	.241	.000	9

EAC = 24000.

DKV = .01

DEX = .005

DALP = .0005

PX = .10

DELH = 7980

VI CONCLUSIONS

Finite-difference equations representing a mathematical model yield complete solutions for each grid point, thus giving a much more detailed description of the proposed model. This feature is of utmost importance when design of equipment is based upon solutions to the mathematical model. Furthermore the use of Parameter-Perturbation enables one to solve large sets of finite-difference equations within a reasonable length of time.

In more detail the use of finite-difference equations and Parameter-Perturbation to solve these equations representing a boundary value problem is to be recommended because:

(1) The algorithm for obtaining the finite-difference equations approximating a boundary value problem and solution of these equations using Parameter-Perturbation is a general one.

(2) Transformation of variables or use of dimensionless parameters is not necessary.

(3) Only measurable physical quantities are required to define the problem.

Note* Numerical accuracy of the calculations carried out by the computer limits the type of problems which can be solved.

VII NOMENCLATURE

A	reactant, Langmuir-Hinshelwood rate expression
A_{ij}	matrix expressing the quantities r_m^P m = 1,2,...,5, P = 0,2,3,4
B	reactant, Langmuir-Hinshelwood rate expression
C	concentration of reactant species
C_x	concentration of reactant X (gm moles/cc)
D	diffusion coefficient (cm^2/sec)
E	activation energy (calories)
$F_i(x_j)$	function of variable x; i = 1,2,...,n, j = 1,2,...,n
$F'_i(x_j)$, $F''_i(x_j)$,...	derivatives of the function $F_i(x_j)$
G_i	incremental value used in parameter-perturbation
K	thermal conductivity of porous catalyst (cal./sec cm K)
K_A	adsorption constant for reactant A (atm^{-1})
K_i	adsorption eonstant for i^{th} species in Langmuir-Hinshelwood rate expression (atm^{-1})
K_o	defined as $(K_A - D_A \sum_i (K_i V_i / D_i))/W$
L	length dimension, cartesian coordinates
L(1), L(X), ...	linear operator, used in derivation of integration formula
P	partial pressure, (atm)

P_{jk}	matrix expressing the 'true' equations parameters
Q_{jk}	matrix expressing the 'derived' equations parameters
Q^{n}_{jk}	matrix expressing the 'perturbed' equations parameters
R	radius of spherical catalyst or radii of cylindrial catalyst
R_g	universal gas constant
S_v	pore surface cm^2/cm^3 of volume of the porous structure
T	temperature in degrees - Kelvin
W	maximum incremental value, equal to one
W_i	constant coefficients of the polynomial integration formula
X	product in Langmuir-Hinshelwood type of rate expression, otherwise the reactant
Y	product in Langmuir-Hinshelwood type of rate expression, otherwise the reactant
b	vector, made up of $\frac{R^P}{P}$, p = 1,2,3,4,5
f(x)	any general function
f(c)	rate mechanism as a function of conc.
h_j	residual of $(x_j - r_j)$
k	reaction rate constant, (g.moles/cc.sec)
k'	modified rate constant, (g.moles atm/cc.sec)
$k_s(T)$	rate constant based on surface area of catalyst (gm.moles/$(cm^2$sec)
$k_v(T)$	rate constant based on volume of the catalyst

m	order of reaction $0 \leq m \leq 1$
r	radii at position r
r_j	j^{th} root of the i^{th} equation, Newton's method
X	dimension in cartesian coordinates
$X_j(1), X_j(2), \ldots$	first, second, etc. approximation to r_j, Newton's method
H	heat of reaction (cal/g mole ^oK)
$\frac{dc}{dr}$ or $\frac{dc}{dx}$	concentration gradient
$\frac{d^2c}{dr^2}$ or $\frac{d^2c}{dx^2}$	gradient of concentration gradient
$\frac{dT}{dr}$ or $\frac{dT}{dx}$	temperature gradient
$\frac{d^2T}{dr^2}$ or $\frac{d^2T}{dx^2}$	gradient of temperature gradient
ε	defined as $\frac{C_{is} \Delta H_i D_r E}{T_s^2 K R_g}$
β	defined as $\frac{C_s \Delta H_i D_r}{T_s K}$
γ	defined as $\frac{E}{R_g T_s}$
ϕ	defined as $L \sqrt{\frac{k_{vs} C_{is}}{D_r}}$

Φ	defined as $(R^2/D_r C_{is})$. (observed reaction rate/gross catalyst volume)
η	defined as the effectiveness factor
η_i	defined as either reaction rate at position n or stoichiometric coefficients
i	index denoting species
j	index denoting position of an element of a matrix
k	index denoting position of an element of a matrix
n	denotes position, or number of the iteration
s	denotes surface

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IX APPENDIX

A DERIVATIONS

(i) Newton's Method

Suppose the following equations are to be solved

(A-1)

$$F_1(x_1, x_2, \ldots, x_n) = 0$$
$$F_2(x_1, x_2, \ldots, x_n) = 0$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$F_n(x_1, x_2, \ldots, x_n) = 0$$

Let r_j, $j = 1,2,\ldots,n$ be the roots in question,

Set $x_j - r_j = h_j$

Then $F_i(r_j) = 0$

Writing a Taylor's series expansion for $F_i(r_j)$

(A-2)

$$0 = F_i(r_j) = F_i(x_j - h_j)$$
$$= F_i(x_j) - h_j F_i'(x_j) + \frac{h_j^2 F_i''(x_j)}{2!} - \ldots$$

If h_j is small, that is, if the choice of x_j is sufficiently accurate, and if the curve $F_i(x_j)$ does not have derivatives at or near x_j so large that they interfere, then an approximate value of h_j obtained by neglecting all but the first two terms in the series is

(A-3)

$$h_j = \frac{F_i(x_j)}{F_i'(x_j)}$$

Then a new approximate value for x_j becomes

(A-4)

$$x_j^{(2)} = x_j^{(1)} - \frac{F_i(x_j^{(1)})}{F_i'(x_j^{(1)})}$$

This procedure is repeated to obtain a better value for $x_j^{(3)}$

$$x_j^{(3)} = x_j^{(2)} - \frac{F_i(x_j^{(2)})}{F_i'(x_j^{(2)})}$$

or in general

(A-5)

$$x_j^{(r)} = x_j^{(r-1)} - \frac{F_i(x_j^{(r-1)})}{F_i'(x_j^{(r-1)})}$$

The procedure converges to a solution for x_j when

$x_j^{(r)} = x_j^{(r-1)} \pm$ specified tolerance.

For calculation purposes an n dimensional problem becomes

$$F_i'(x_j^{(d-1)})\ x_j^{(d)} = F_j'(x_j^{(d-1)})\ x_j^{(d-1)} - F_i(x_{j-1}^{(d-1)})$$

or in matrix form

(A-6)

$$\underline{F'(x^{(d-1)})} \cdot \underline{x^{(d)}} = \underline{F'(x^{(d-1)})\ x^{(d-1)} - F(x^{(d-1)})}$$

Nomenclature employed

$F_i(x_j)$ equation to be solved; i = 1,2,...,n; j = 1,2,...,n

$F'_i(x_j)$ first derivative of $F_i(x_j)$

$F''(x_j)$ second derivative of $F_i(x_j)$

$x_j^{(1)}$ first approximation to true solution

$x_j^{(d)}$ d^{th} approximation to true solution

(ii) Derivation of Finite-Difference Equations

By using equations (3-15) to (3-18) inclusive it is possible to derive the general finite-difference equations representing the energy balance for spherical coordinates.

For n = 1,2,3,...,n-1, the energy equation is;

(A-7)

$$\frac{T_{n+1} - 2T_n + T_{n-1}}{\Delta r^2} + \frac{2}{m\Delta r}\frac{(2T_{n+1} + 3T_n - 6T_{n-1} + T_{n-2}}{6\Delta r}$$

$$-\sum_i H_i f_i(C_A, C_B, \ldots, T) = 0$$

For n = N, the energy equation is;

(A-8)

$$- \frac{T_{N-2} + 10T_{N-1} - 25T_N + 16T_S}{5\Delta r^2} + \frac{2}{m\Delta r}\left(\frac{3T_{N-2} - 20T_{N-1} - 15T_N + 32T_S}{30\Delta r}\right)$$

$$- \sum_i H_i f_i(C_A, C_B, \ldots, T) = 0$$

where $m\Delta r = r$

By using equations (3-19) to (3-22) inclusive, we can derive the general finite-difference equations representing the mass balance in spherical coordinates.

For n = 1,2,3,...,n-1, the mass equation;

(A-9)

$$\frac{C_{i,n+1} - 2C_{i,n} + C_{i,n-1}}{\Delta r^2} + \frac{2}{m\Delta r}\left(\frac{2C_{i,n+1} + 3C_{i,n} - 6C_{i,n-1} + C_{i,n-2}}{6\Delta r}\right)$$

$$- f_i(C_A, C_B, \ldots, T) = 0$$

For n = N, the mass equation is;

(A-10)

$$- \frac{C_{i,N-2} + 10C_{i,N-1} - 25C_{i,N} + 16C_{i,S}}{5\Delta r^2} +$$

$$\frac{2}{m\Delta r}\left(\frac{3C_{i,N-2} - 20C_{i,N-1} - 15C_{i,N} + 32C_{i,S}}{30\Delta r}\right) -$$

$$f_i(C_A, C_B, \ldots, T) = 0$$

(iii) Calculation of Overall Effectiveness Factor

We want to numerically evaluate the integral;

(A-11)

$$\eta = \int_0^R \frac{3r^2 \jmath \, dr}{R^3 \jmath_R}$$

where $\jmath$ is the rate of reaction at grid point n.

Assume we want to approximate the function by passing a fourth degree polynomial through any five known points on the radii. This requirement enables one to develop a formula which has the following form;

(A-12)

$$\int_0^N f(x)dx = \sum_0^4 W_n f(x_n) + \ldots + \sum_{n=N-4}^N W_n f(x_n)$$

where W_n are the constants to be determined.

For any set of known five grid points using a total interval of one with $x_i = r_i$ we obtain the following linear matrix;

(A-13)

$$L(1) = W_1 + W_2 + W_3 + W_4 + W_5 = 1$$

$$L(x) = W_1 r_1 + W_2 r_2 + W_3 r_3 + W_4 r_4 + W_5 r_5 = \frac{1}{2}$$

$$L(x^2) = W_1 r_1^2 + W_2 r_2^2 + W_3 r_3^2 + W_4 r_4^2 + W_5 r_5^2 = \frac{1}{3}$$

$$L(x^3) = W_1 r_1^3 + W_2 r_2^3 + W_3 r_3^3 + W_4 r_4^3 + W_5 r_5^3 = \frac{1}{4}$$

$$L(x^4) = W_1 r_1^4 + W_2 r_2^4 + W_3 r_3^4 + W_4 r_4^4 + W_5 r_5^4 = \frac{1}{5}$$

For uniform grid spacing r_1 to r_5 take on the values 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and 1 respectively. For a grid spacing consisting of a one-half unit and three even units r_1 to r_5 take on the values 0, $\frac{1}{7}$, $\frac{3}{7}$, $\frac{5}{7}$, and 1 respectively.

Let $\underline{A}$ represent $f(r_{jk})$, $j = 1,2,\ldots,5$; $k = 1,2,\ldots,5$

$\underline{W}$ represent the required weighting factors

$\underline{b}$ represent $\frac{R}{P}^P$, $P = 1,2,\ldots,5$; $R = 1$

(A-14)

Then $\underline{W} = \underline{b}\ \underline{A}^{-1}$

When $\underline{W}$ is obtained, its elements are multiplied by the total interval which the corresponding five points represent. Then since $\underline{W}_5^{(m)}$ and $\underline{W}_1^{(m+1)}$ represent the same grid point, they are combined. The weighting factors are now in the form in which they can be used for the problem we are about to solve. Equation (A-11) then becomes;

(A-15)

$$\eta_o = \frac{3}{R\rho_R} \left(W_1 \rho_1 r_1^2 + W_2 \rho_2 r_2^2 + \ldots + W_N \rho_N R_N^2 \right)$$

where subscript N indicates the n^{th} vector.

(iv) Temperature Dependent Rate Constant

The expression

$$k_v \; T^m e^{\frac{-E}{R_g T}} \qquad 0 \leq m \leq 1 \tag{A-16}$$

summarizes the predictions of the simpler versions of the various theories for the temperature dependency of the rate constant. Because the exponential term is so much more temperature - sensitive than the T^m term, the variations of k_v caused by the latter is effectively masked, this results in

$$k_v = k_s e^{\frac{-E}{R_g T}} \tag{A-17}$$

For computational purposes, k_s must be eliminated, the reason being that the computer cannot accurately calculate the difference of two number of the order of $e^{(30)}$.

(A-18)

thus

$$k_v = k_{vs} e^{\left(\frac{E}{R_g T_s} - \frac{E}{R_g T}\right)}$$

B NUMERICAL EXAMPLE PROBLEM

To show the applicability of Parameter-Perturbation using Newton's method, we chose to solve a non-linear system of algebraic finite-difference equations found in detail in the book by Lapidus, (8). Lapidus made use of a quadratic forcing technique to obtain solutions to the finite-difference equations, but the rate of convergence using this technique is very slow.

Following is an outline of the problem.

Given the finite-difference representation of a second-order reaction taking place in a fluid flowing through a tubular reactor in laminar flow, we want to solve for the concentration of the reactant as a function of the dimensionless distance.

The boundary conditions are:

(B-1)

$$1 = f_o - \frac{1}{Peh}(f_1 - f_o) \qquad \text{at } Z = 0$$

$$f_N = f_{N+1} \qquad \text{at } Z = 1$$

where:

- f_i represents the concentration of the reactant, $i = 1,2,\ldots,N$
- h represents the dimensionless distance segment
- N represents the total number of grid points
- Pe represents the Peclet number
- Z represents the dimensional distance

The specified input parameters are:

h = .04

N = 24.

Pe = 1.0

R = 2.0

where R is the Reynolds number

A system of twenty-four algebraic finite-difference equations having the following form can be generated.

(B-2)

$$2 - \frac{1+Peh/2}{1+Peh} f_1 + RPeh^2 f_1^2 - (1-Peh/2) f_2 - \frac{1+Peh/2}{1+Peh} = 0$$

$$- (1+Peh/2) f_1 + 2.0 f_2 + RPeh^2 f_2 - (1-Peh/2) f_3 = 0$$

$$- (1+Peh/2) f_{n-1} + 2.0 f_n + RPeh^2 f_n^2 - (1-Peh/2) f_{n+1} = 0$$

$$- (1+Peh/2) f_{23} + (1+Peh/2) f_{24} + RPeh^2 f_{24} = 0$$

This system of twenty-four non-linear equations were solved on the I.B.M. 7040 computer using Parameter-Perturbation with Newton's method. Trial vectors used were $\underline{F}^{(o)} = (1.0)$ and $\underline{F}^{(o)} = (0.0)$. For $\underline{F}^{(o)} = (1.0)$ Newton's method by itself was satisfactory, for $\underline{F}^{(o)} = (0.0)$ one set of 'perturbed' equations had to be solved before the true solution to the system was obtained. A comparison of results obtained by

Parameter-Perturbation versus results obtained by Lapidus is presented in Table 4, page 53. Complete results are found in Table 5, page 54.

TABLE 4 Comparison of Results, Example Problem

Grid Point	Parameter-Perturbation Results	Lapidus' Results	% Difference
5	.577403	.577406	.0005
10	.528069	.528072	.0006
15	.492703	.492705	.0004
20	.471153	.471155	.0004

where % difference is calculated as

$$\frac{\text{Lapidus' Results - Parameter-Perturbation Results}}{\text{Parameter-Perturbation Results}} \times 100$$

TABLE 5 Complete Results, Example Problem

Trial Vector	Number of Sets of Perturbed Equations Required	Solution to the Set of Finite-Difference Equations	Object Time IBM 7040
$\underline{F}^{(o)} = 1.00$	0	.627874	4 seconds
		.614265	
		.601332	
		.589052	
		.577403	
		.566368	
		.555930	
		.546075	
		.536791	
		.528069	
		.519902	
		.511228	
		.505212	
		.498685	
		.498685	
		.492703	
		.487270	
		.482390	
		.478070	
		.474321	
		.471153	
		.468581	
		.466620	
		.465290	
		.465290	
$\underline{F}^{(o)} = 0.00$	1	Same as those for 7 seconds $\underline{F}^{(o)} = 1.000$	

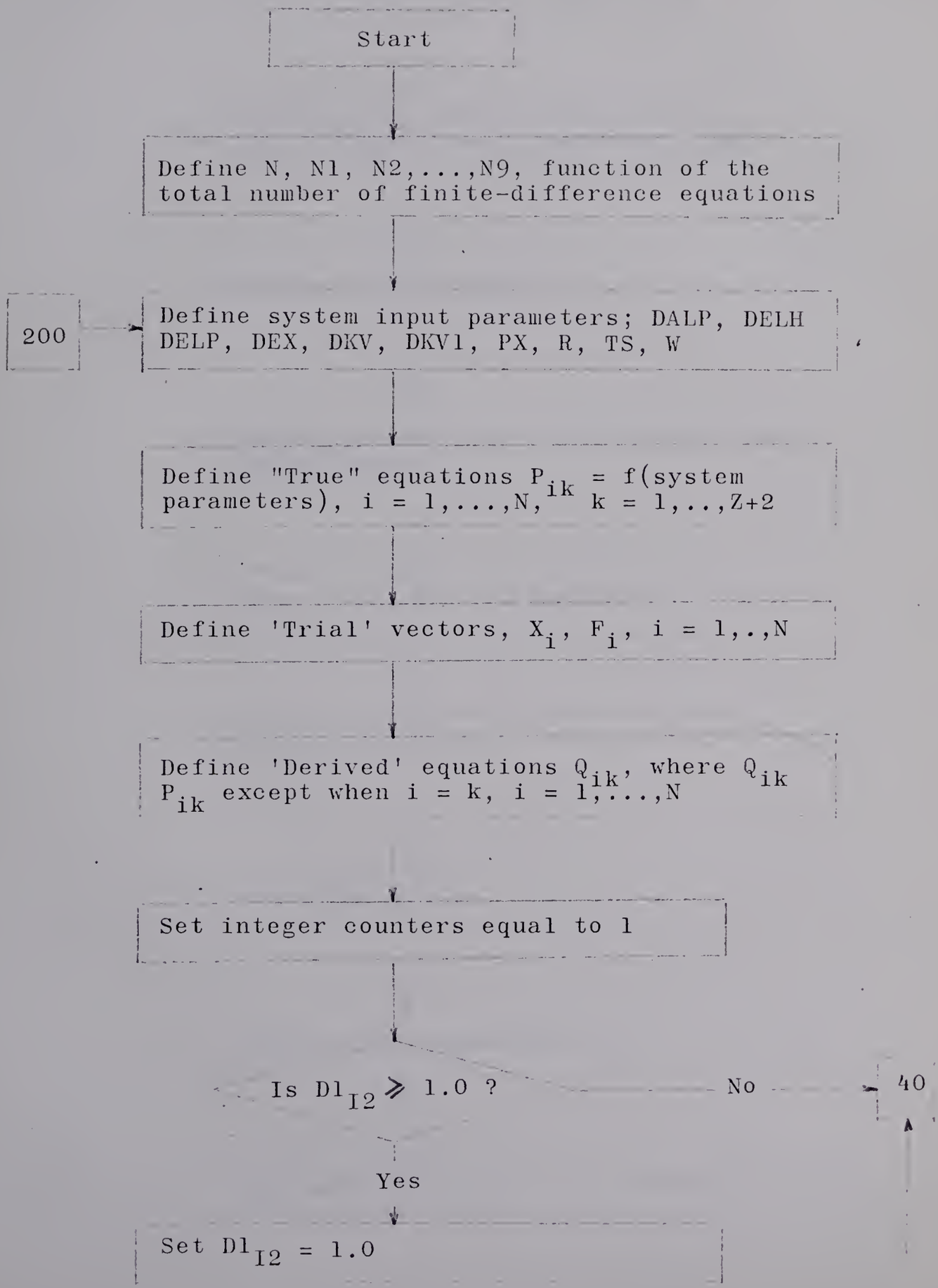
From Table 4, page53 and Table 5, page 54 it is noted that,

(1) Newton's method increases the rate at which convergence is obtained as compared to the 801 iterations required by the quadratic forcing technique.

(2) Parameter-Perturbation enables one to use any physically possible initial trial vector.

(3) Calculation time is small, 4 to 7 seconds on an IBM 7040 computer, compared to Lapidus method which, took 40 seconds per 100 iterations on an IBM 701 computer.

C GENERAL FLOW DIAGRAM



40 → Calculate Ql_{ik}, where Ql_{ik} is defined as $Ql_{ik} = Q_{ik} + {}^{jk}(P_{ik} - Q_{ik})^{jk}Dl_{I2}/W$ ← 100

↓

41 → Evaluate the partial derivatives, $A_{ik} = (f(\text{perturbed equations})_i)/X_k$

↓

Evaluate the residuals G_i, i = 1,...,N

↓

Calculate and store the absolute sum of the residuals

↓

Calculate R,H.S. of matrix A

↓

Increase Il by 1

↓

Solve for X_i^{n+1}

↓

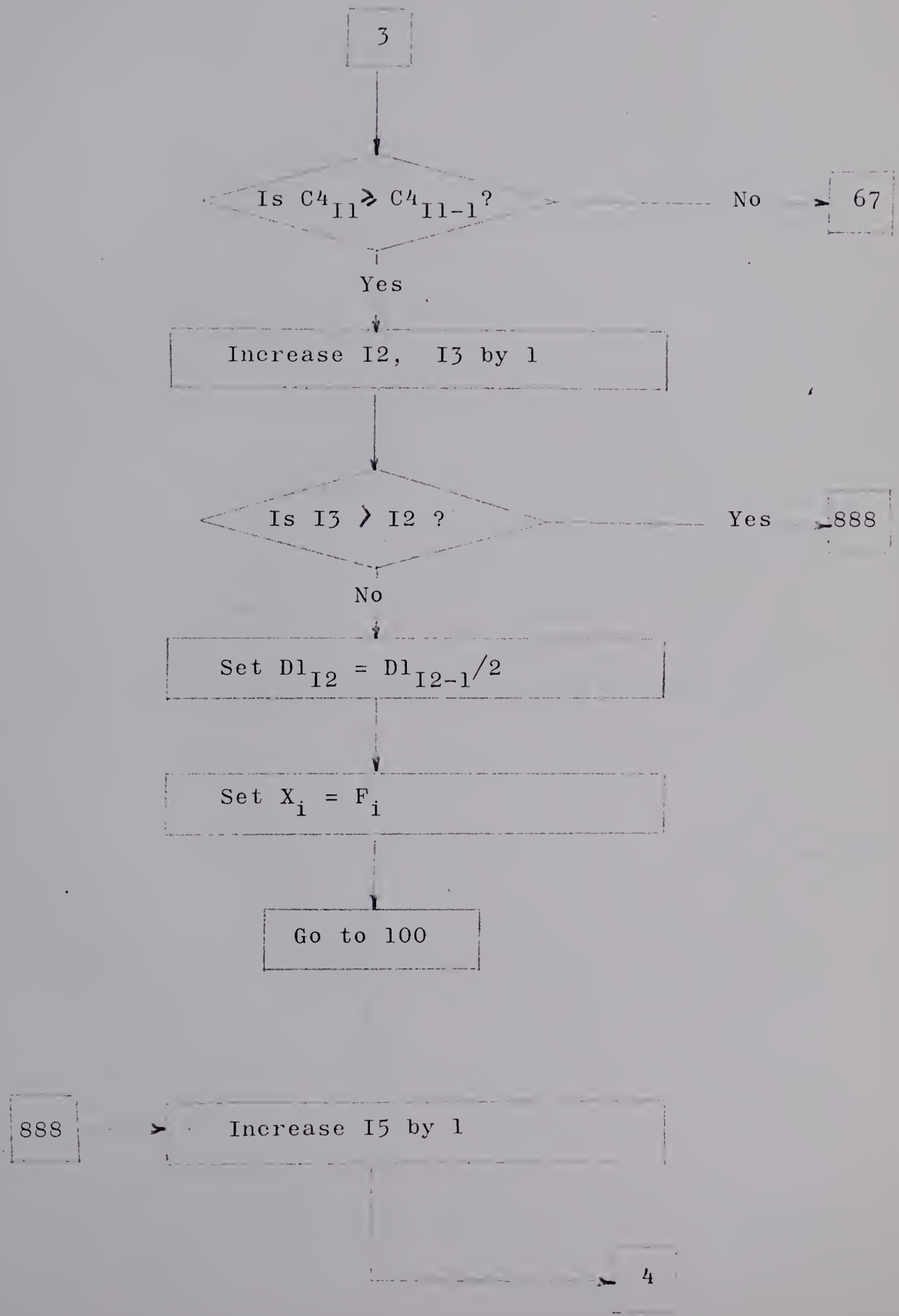
Evaluate the residuals G_i, i = 1,...,N

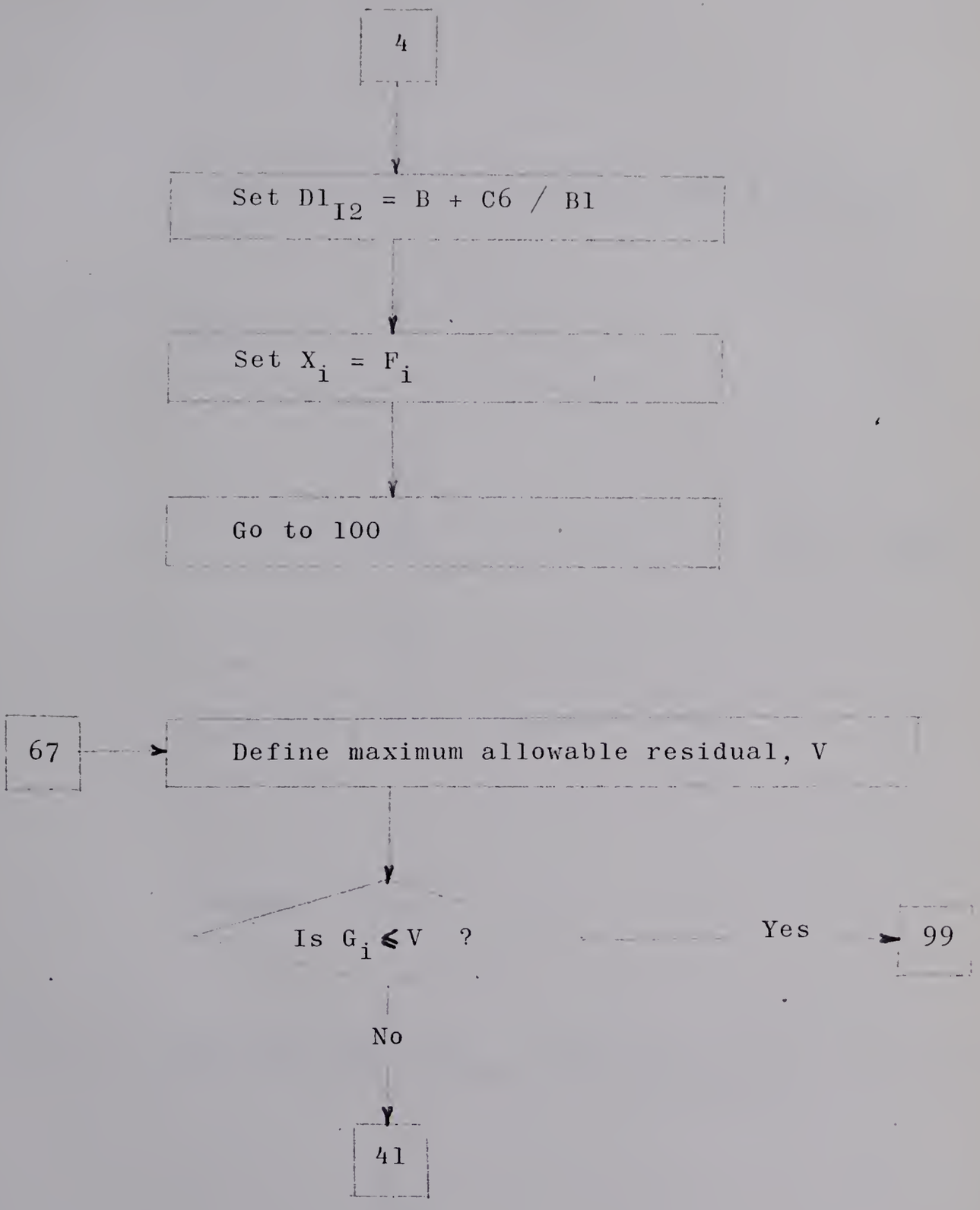
↓

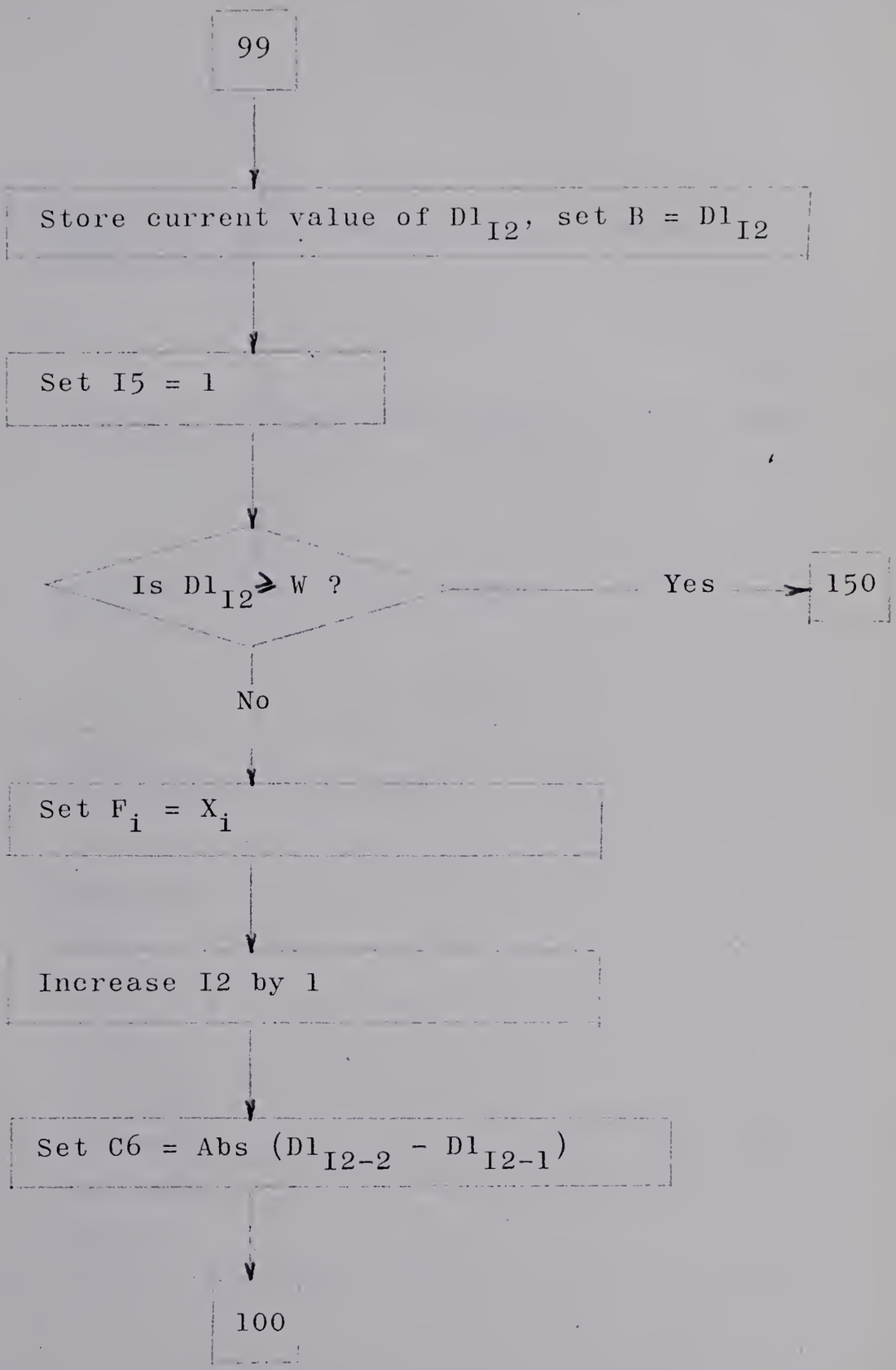
Calculate and store the residuals

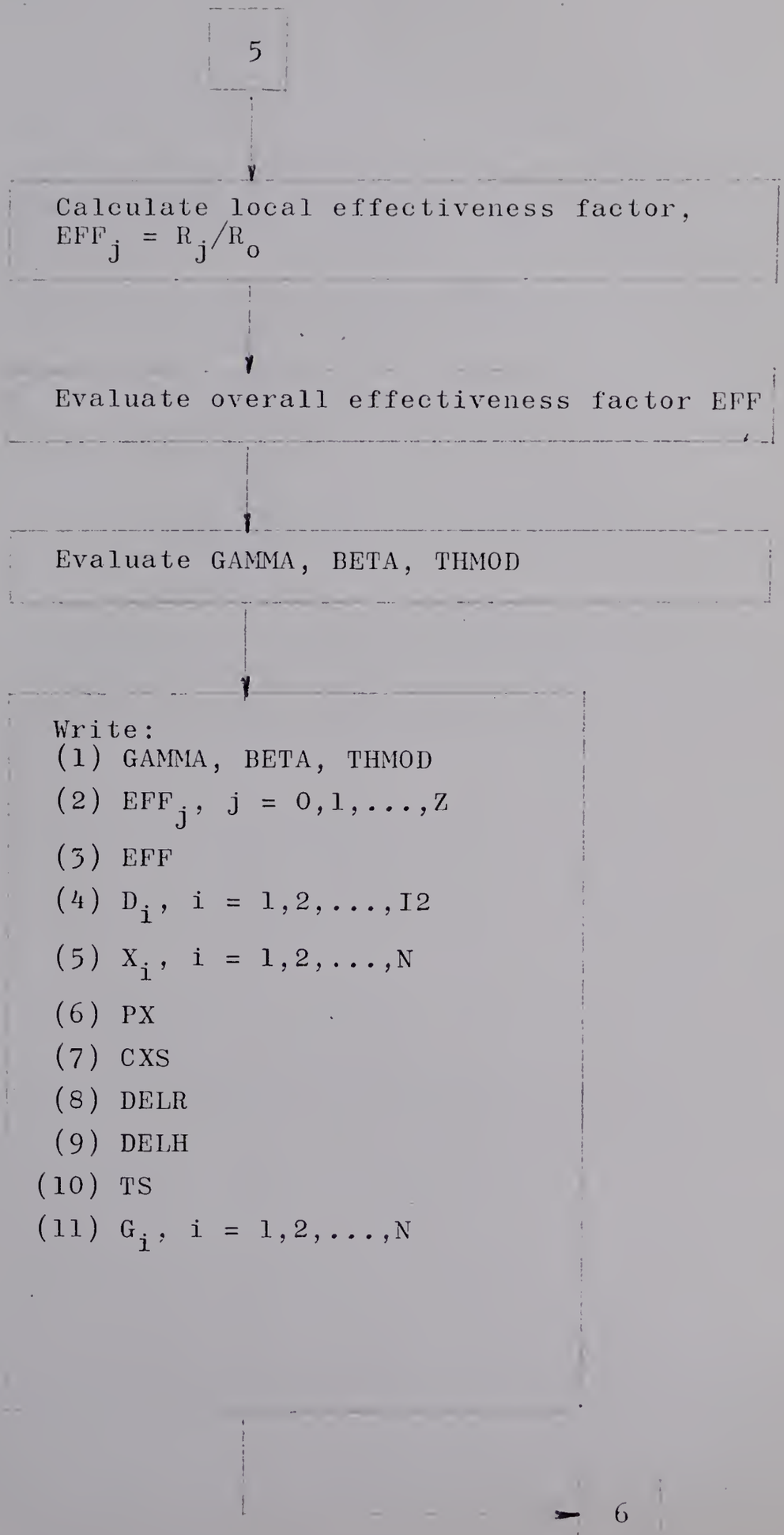
↓

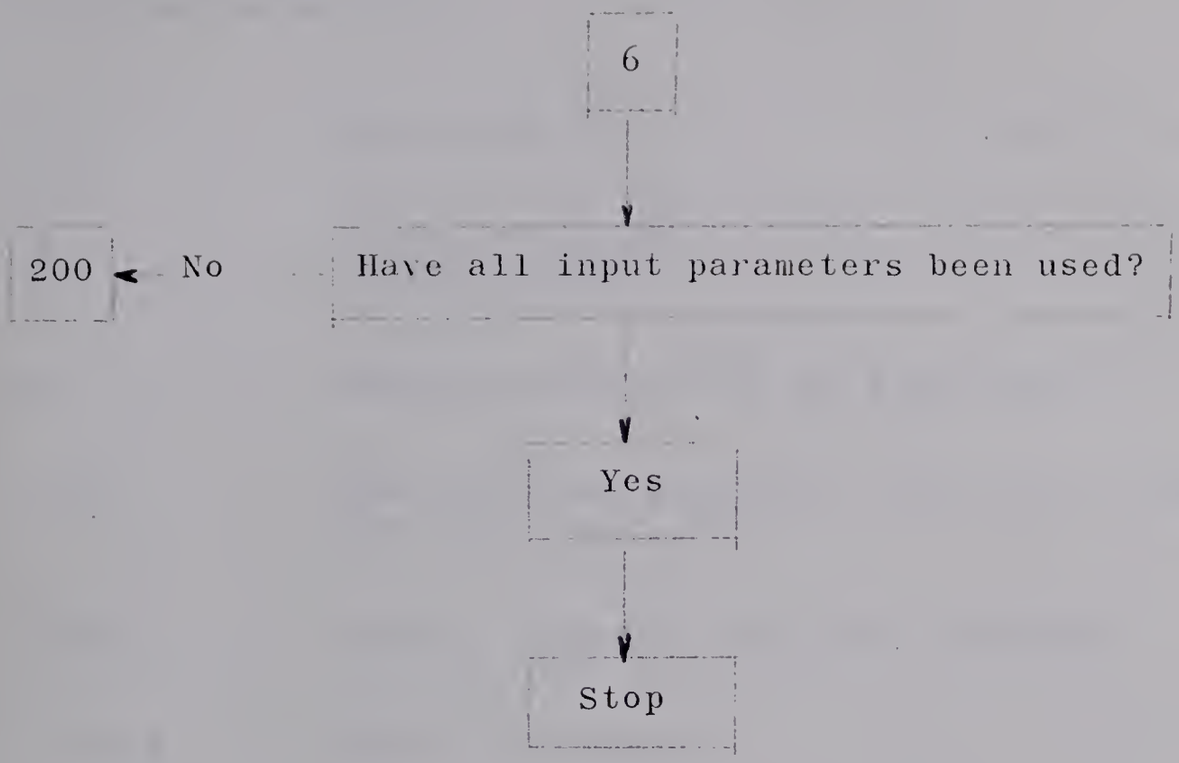
→ 3


3
Is $C4_{I1} \geq C4_{I1-1}$?
No
67
Yes
Increase I2, I3 by 1
Is I3 > I2 ?
Yes
888
No
Set $Dl_{I2} = Dl_{I2-1}/2$
Set $X_i = F_i$
Go to 100
888
Increase I5 by 1
4


4
Set $D1_{I2}$ = B + C6 / B1
Set $X_i = F_i$
Go to 100
67
Define maximum allowable residual, V
Is $G_i \leq V$?
Yes
99
No
41


99
Store current value of Dl_{I2}, set B = Dl_{I2}
Set I5 = 1
Is $Dl_{I2} \geq W$?
Yes
150
No
Set $F_i = X_i$
Increase I2 by 1
Set C6 = Abs $(Dl_{I2-2} - Dl_{I2-1})$
100
150
Calculate rate of reaction at surface and all interior points R_j, j = 0,1,...,Z
5


5
Calculate local effectiveness factor, $EFF_j = R_j/R_o$
Evaluate overall effectiveness factor EFF
Evaluate GAMMA, BETA, THMOD
Write:
(1) GAMMA, BETA, THMOD
(2) EFF_j, j = 0,1,...,Z
(3) EFF
(4) D_i, i = 1,2,...,I2
(5) X_i, i = 1,2,...,N
(6) PX
(7) CXS
(8) DELR
(9) DELH
(10) TS
(11) G_i, i = 1,2,...,N
6


6
Have all input parameters been used?
No
200
Yes
Stop

Program Nomenclature

A_{IJ}	Partial derivatives, I = 1, ...,N; J = 1, ...,N
B	Value of increment D1(I2), most recent point of convergence
B1	Present value of 15, in fixed mode
BETA	Dimensionless parameter, function of (DELH, CXS, DEX, DALP, TS)
CXS	Surface concentration of X component
C4(I1)	Sum of residuals
DALP	Thermal conductivity of catalyst particle
DELH	Heat of reaction
DELR	Incremental radii, squared
DEX	Effective diffusion constant, component X
DKV	Rate constant at surface conditions
DKV1	Effective adsorption constant
D1(I2)	Incremental value, $0 \leq D1(I2) \leq 1$
EAC	Activation energy

EFF	Overall effectiveness factor
EFF(I)	Local effectiveness factor(s), I =1, 2, ..., Z
EK	Defined as EAC/(RG TS)
F_I	Most recent correct solution to 'perturbed' equations
GAMMA	Same as EK
I, J, K	Integer variables
IK,I2,I3,I5	Integer counter, used for convergence procedure
L1, L2, ...	Integer variables, used for parameter variations
N	Number of finite-difference equations
P_{IK}	Parameter of finite-difference equations representing the physical problem, I = 1, 2, ..., N; K = 1, 2, ..., Z+2
PC	Proportionality constant
PT	Total pressure of system
PX	Partial pressure of X component
Q_{IK}	Parameters of 'derived' equations, I = 1, 2, ..., N; K = 1, 2, ..., Z+2

$Q1_{IK}$	Parameters of 'perturbed' equations, defined as $Q1_I$, $K = Q_{IK} + (P_{IK} - Q_{IK})$ D1(I2)/W, $I = 1, 2, \ldots, N$; $K = 1, 2, \ldots, Z+2$
RG	Gas constant, either 1.087 or 82.1
R	Radii of spherical catalyst
THMOD	Modified Thiele Modulus
TS	Surface temperature
V	Specified maximum residual size
W	Maximum incremental value
X_I	Approximate solution to present set of 'perturbed' equations
Z	Number of grid points used in finite-difference representation

D. TABULATED RESULTS

(i) First Order System

Type of Computer	IBM 7040
Number of Sets of Solutions Obtained	22
Number of Grid Points Employed, Spherical	23
Object Time	9 min. 45 sec.
Fortran Time	3 min. 41 sec.

Type of Computer	IBM 7040
Number of Sets of Solutions Obtained	24
Number of Grid Points Employed, Spherical	19
Object Time	10 min., 1 sec.
Fortran Time	3 min. 26 sec.

(ii) Langmuir-Hinshelwood System

Type of Computer	IBM 7040
Number of Sets of Solutions Obtained	12
Number of Grid Points Employed, Spherical	23
Object Time	8 min. 52 sec.
Fortran Time	3 min. 34 sec.

Type of Computer	IBM 7040
Number of Sets of Solutions Obtained	15
Number of Grid Points Employed, Spherical	19
Object Time	5 min. 34 sec.
Fortran Time	3 min. 6 sec.

Type of Computer	IBM 7040
Number of Sets of Solutions Obtained	15
Number of Grid Points Employed, Slab	19
Object Time	6 min. 18 sec.
Fortran Time	3 min. 10 sec.

(iii) Example of Computer Output

System Parameters

Gamma	30.0	Beta	0.00	Th.Mod.	1.79	P_{xs}	10.0
C_{xs}	.003	Delr	.0019	Delh	0.00	T_s	402.6
Dex	.005	Dalp	.0005	Dkv	.01		

Overall Effectiveness Factor .88901

Number of Increments 1.00

Position $\frac{r}{R}$	Local Effectiveness Factor	Concentration $\frac{C}{C_s}$	Temperature $\frac{T}{T_s}$
1/46	.7309	.73097	1.00000
3/46	.7319	.73189	1.00000
5/46	.7337	.73373	1.00000
7/46	.7365	.73651	1.00000
9/46	.7402	.74021	1.00000
11/46	.7448	.74486	1.00000
13/46	.7504	.75046	1.00000
15/46	.7570	.75703	1.00000
17/46	.7646	.76458	1.00000
19/46	.7731	.77313	1.00000
21/46	.7827	.78269	1.00000
23/46	.7933	.79329	1.00000
25/46	.8049	.80496	1.00000
27/46	.8177	.81771	1.00000
29/46	.8316	.83159	1.00000
31/46	.8466	.84662	1.00000
33/46	.8628	.86283	1.00000
35/46	.8803	.88027	1.00000
37/46	.8990	.89897	1.00000
39/46	.9190	.91898	1.00000
41/46	.9403	.94034	1.00000
43/46	.9631	.96311	1.00000
45/46	.9873	.98733	1.00000

Residuals $\leq$ .00001

(IV) Summary of Results

Reaction Mechanism	β	Δ	Φ	η
First Order (Spherical - Coordinates)	0.00	30.0	1.778	.889
	0.00	30.0	4.467	.745
	0.00	30.0	6.537	.654
	0.00	30.0	8.263	.590
	0.00	30.0	9.769	.543
	0.00	30.0	11.120	.505
	0.00	30.0	12.356	.475
	0.00	30.0	13.501	.450
	0.00	30.0	14.574	.429
	0.00	30.0	15.587	.410
	-.20	30.0	1.275	.638
	-.20	30.0	2.736	.456
	-.20	30.0	3.794	.380
	-.20	30.0	4.669	.333
	-.20	30.0	5.432	.302
	-.20	30.0	6.119	.278
	-.20	30.0	6.746	.259
	-.20	30.0	7.329	.244
	-.20	30.0	7.875	.232
	-.20	30.0	8.390	.221
	+.05	30.0	2.108	1.054
	+.05	30.0	6.006	1.001

Reaction Mechanism	$P_{As}K_o$	Φ	η
Langmuir-Hinshelwood (Spherical - Coordinates)	-.964	7.798	.135
	-.964	4.073	.212
	-.964	2.968	.257
	-.964	2.396	.291
	-.964	2.036	.318
(Linear - Coordinates)	-.964	3.020	.0524
	-.964	1.750	.0910
	-.964	1.330	.116
	-.964	1.110	.135
	-.964	.969	.151

(v) Fortran Source List

Following is a summary of a general program utilizing Parameter-Perturbation to solve the rate expression

$$r_i = k_i P_i / (1+K_A P_i)$$

Program 1 is for spherical coordinates, Program 2 is for a slab. All input parameters must be specified as well as the number of grid points to be employed.

Since Programs 1 and 2 are quite similar, Program 2 consists of only a list of cards which are different. Unless stated otherwise assume the cards are interchangeable.

CARD NUMBER	STATEMENT NUMBER	STATEMENT
1		GRID = 15 OR 19 OR 23 OR ....
2		N4 = GRID
3		N1 = 2 * N4
4		N2 = N4 + 2
5		N3 = N4 + 1
6		N5 = N4 - 1
7		N6 = N1 - 1
8		N7 = N4 + 3
9		N8 = N1 + 1
10		N9 = N4 - 2
11		NN1 = N1 - 2
12	1	FØRMAT (1X,514.8)
13		READ (5,1)TS,DELH,EAC,RG,PX
14		READ (5,1)PC,DALP,DEX,DKV,DKV1
15		CXS = PX/(RG * TS)
16		EK = EAC/(1.987 * TS)
17		DKØ = DKV
18		Z = PC * DEX/(RG * TS)
19		DN1 = N1
20		DN6 = N6
21		DR = 2./DN1
22		DELR = DR * * 2
23		DIMENSION P(N1,N2), X(N1), F(N1)
24		P(1,1) = Z*(-1./DELR+2.*DN1*(-3./(6.*DR)))
25		P(1,2) = -P(1,1)
26		P(2,1) = Z*(1./DELR+2.*DN1/3.*(-5./(6.*DR)))
27		P(2,2) = Z*(-2./DELR+2.*DN1/3.*(3./(6.*DR)))
28		P(2,3) = Z*(1./DELR+2.*DN1/3.*(2./(6.*DR)))
29		DØ 508 I = 3, N5

CARD NUMBER	STATEMENT NUMBER	STATEMENT
30		Z1 = I
31		Z2 = 2.*Z1 - 1.
32		P(I,I-2) = Z*(2.*DN1/Z2*(1./(6.*DR)))
33		P(I,I-1) = Z8(1./DELR+2.*DN1/Z2*(-6./(6.*DR)))
34		P(I,I) = Z*(-2./DELR+2.*DN1/Z2*(3./(6.*DR)))
35		P(I,I+1) = Z*(1./DELR+2.*DN1/Z2*(2./(6.*DR)))
36	508	CØNTINUE
37		P(N4,N9) = Z*(-1./(5.*DELR)+2.*DN1/DN6*(3./(30.*DR)))
38		P(N4,N5) = Z*(10./(5.*DELR)+2.*DN1/DN6*(-20./(30.*DR)))
39		P(N4,N4) = Z*(-25./(5.*DELR)+2.*DN1/DN6*(-15./(30.*DR)))
40		DØ 557 I = N3, N1
41		DØ 557 J= 1, N4
42		L1 = I - N4
43	557	P(I,J) = P(L1,J)*TS*DALP*RG/(PC*DEX)
44		P(N4,N2) = Z*(16./(5.*DELR)+2.*DN1/DN6*(32./(30.*DELR)))*PX
45		P(N1,N2) = TS*DALP*(16./(5.*DELR)+2.*DN1/DN6*(32./(50.*DR)))
46		P(1,N3) = - PC*DKV
47		DØ 701 K = 2, N4
48	701	P(K,N3) = P(1,N3)
49		P(N3,N3) = DKO * DELH
50		DØ 703 K = N2, N1
51	703	P(K,N3) = P(N3, N3)
52		DØ 197 I = 1. N4
53	197	F(I) = PX
54		DØ 188 I = N3, N1
55	188	F(I) = 1.00000
56		DØ 157 I = 1, N1

CARD NUMBER	STATEMENT NUMBER	STATEMENT
57	157	X (I) = F(I)
58		DIMENSION Q(N1,N2), Q1(N1,N2), D1(50)
59		DØ 107 I = 1, N1
60		DØ 107 J = 1, N2
61	107	Q(I,J) = P(I,J)
62		Q(1,1) = (Q(1,2)*X(2)+Q(1,N3)*X(1)/ (1.+DKV1*X(1)))/X(1)
63		Q(2,2) = -(Q(2,1)*X(1)+Q1(2,3)*X(3) +Q(2,N3)*X(2)/(1.+DKV1*X(2)))/X(2)
64		DØ 110 I = 3, N5
65		Q(I,I) = - (Q(I,I-2)*X(I-2)+Q(I,I-1) *X(I-L)+Q(I,I+1)*X(I+1)+Q(I,N3)*X(I)/ (1.+DKV1*X(I)))/X(I)
66		Q(N4,N4) = -(Q(N4,N4-2)*X(N4-2)+Q(N4, N4-1)*X(N4-1)+Q(N4,N2)+Q(N4,N3)*X(N4)/ (1.+DKV1*X(N4)))/X(N4)
67		Q(N3,1) = -(Q(N3,2)+Q(N3,N3)*X(1)/ (1+DKV1*X(1)))
68		Q(N2,2) = -(Q(N2,1)=Q(N2,3)+Q(N2,N3)* X(2)/(1.+DKV1*X(2)))
69		DØ 112 I = N7, N6
70		L2 = I - N2
71		L3 = I - N3
72		L4 = I - N5
73		L5 = I - N4
74	112	Q(I,L5) = -(Q(I,L2)+Q(I,L3)+Q(I,L4)+ Q(I,N3)*X(L5)/(1.+DKV1*X(L5)))
75		Q(N1,N4) = -(Q(N1,N4-2)+Q(N1,N4-1)+ Q(N1,N4+2)+Q(N1,N3)*X(N4)/(1.+DKV1*X(N4)))
76		I2 = 1
77		I3 = 1
78		I5 = 1
79		D1(I2) = 1.00000

CARD NUMBER	STATEMENT NUMBER	STATEMENT
80	100	CØNTINUE
81		I1 = 1
82		IF(D1(I2).GT.W)GØ TØ 999
83		GØ TØ 998
84	999	D1(I2) = 1.00000
85	998	CØNTINUE
86	C	EVALUATING THE PRESENT DERIVED CONSTANTS
87		DØ 30 I = 1,N1
88		DØ 30 K = 1,N2
89	30	Q1(I,K) = Q(I,K)+(P(I,K)-Q(I,K))*D1(I2)
90	40	CØNTINUE
91	C	EVALUATING THE PARTIAL DERIVATIVES
92		DIMENSION A(N1,N8)
93		A(1,2) = Q1(1,2)/X(N2)
94		A(1,N2) = -Q1(1,2)*X(2)/X(N2)**2
95		A(2,1) = Q1,(2,1)/X(N3)
96		A(2,3) = Q1(2,3)/X(N3+2)
97		A(2,N3) = -Q1(2,1)*X(1)/X(N3)**2
98		A(2,N3+2) = -Q1(2,3)*X(3)/X(X(N3+2)**2
99		DØ 850 I = 3, N5
100		L2 = I + N9
101		L3 = I + N5
102		L4 = I + N3
103		A(I,I-2) = Q1(I,I-2)/X(L2)
104		A(I,I-1) = Q1(I,I-1)/X(L3)
105		A(I,L3) = -Q1(I,I-1)*X(I-1)/X(L3)**2
106		A(I,L2) = -Q1(I,I-2)*X(I-2)/X(L2)**2
107		A(I,I+1) = Q1(I,I+1)/X(L4)
108	850	A(I,L4) = -Q1(I,I+1)*X(I+1)/X(L4)**2
109		A(N4,N4-2) = Q1(N4,N4-2)/X(N1-2)

CARD NUMBER	STATEMENT NUMBER	STATEMENT
110		A(N4,N1-2) = Q1(N4,N4-2)*X(N4-2)/X(N1-2) **2
111		A(N4,N4-1) = Q1(N4,N4-1)/X(N1-1)
112		A(N4,N1-1) = -Q1(N4,N4-1)*X(N4-1)/ X(N1-1)**2
113		DØ 668 I = 1, N4
114		L2 = I + N4
115		A(I,I) = Q1(I,I)/X(L2)+Q1(I,N3)*((1.+DKV1*X(I))*EXP(EK-EK/X(L2))- DKV1*EXP(EK-EK/X(L2))*X(I))/ (1.+DKV1*X(I))**2)
116	668	A(I,L2) = Q1(I,N3)*((X(I)*EXP(EK-EK/ X(L2))*EK/X(L2)**2)/(1.+DKV1*X(I)))- Q1(I,I)*X(I)/X(L2)**2
117		DØ 669 I = N3, N1
118		L2 = I - N4
119		A(I,L2) =Q1(I,N3)*(((1.+DKV1*X(L2))* EXP(EK -EK/X(I))-DKV1*EXP(EK-EK/X(I)) *X(L2))/(1.+DKV1*X(L2))**2)
120	669	A(I,I) = Q1(I,L2)+Q1(I,N3)*((X(L2)* EXP(EK-EK/X(I))*EK/X(I)**2)/(1.+DKV1* X(L2)))
121		A(N3,N2) = Q1(N3,2)
122		A(N2,N3) = Q1(N2,1)
123		A(N2,N7) = Q1(N2,3)
124		DØ 779 I = N7, N6
125		L2 = I - N2
126		L3 = I - N3
127		L4 = I - N5
128		A(I,I-2) = Q1(I,L2)
129		A(I,I-1) = Q1(I,L3)
130	779	A(I,I+1) = Q1(I,L4)
131		A(N1,N1-2) = Q1(N1,N4-2)
132		A(N1,N1-1) = Q1(N1,N4-1)

CARD NUMBER	STATEMENT NUMBER	STATEMENT
133	C	EVALUATING THE RESIDUALS
134		G(1) = Q1(1,1)*X(1)/X(N3)+Q1(1,2)* X(2)/X(N2)+Q1(1,N3)*EXP(EK-EK/X(N3)) *X(1)/(1.+DKV1*X(1))
135		G(2) = Q1(2,1)* X(1)/X(N3)+Q1(2,2)* X(2)/X(N2)+Q1(2,3)*X(3)/X(N7)+Q1 (2,N3)*EXP(EK-EK/X(N2))*X(2)/(1.+ DKV1*X(2))
136		DØ 885 I = 3, N5
137		L2 = I + N9
138		L3 = I + N5
139		L4 = I + N4
140		L5 = I + N3
141	885	G(I) = Q1(I,I-2)*X(I-2)/X(L2)+Q1 (I,I-1)*X(I-1)/X(L3)+Q1(I,I)*X(I) /X(L4)+Q1(I,I+1)*X(I+1)/X(L5)+Q1 (I,N3)*EXP(EK-EK/X(L4))*X(I)/(1.+ DKV1*X(I))
142		G(N4) = Q1(N4,N4-2)*X(N4-2)/X(N1-2) +Q1(N4,N4-1)*X(N4-1)/X(N1-1)+Q1(N4, N4)*X(N4)/X(N1)+Q1(N4,N2)+Q1(N4,N3) *EXP(EK-EK/X(N1))*X(N4)/(1.+DKV1* X(N4))
143		G(N3) = Q1(N3,1)*X(N3)+Q1(N3,2)*X(N2) +Q1(N3,N3)*EXP(EK-EK/X(N3))*X(1)/ (1.+DKV1*X(1))
144		G(N2) = Q1(N2,1)*X(N3)+Q1(N2,2)*X(N2) +Q1(N2,3)*X(N7)+Q1(N2,N3)*EXP(EK-EK/ X(N2))*X(2)/(1.+DKV1*X(2))
145		DØ 889 I = N7, N6
146		L2 = I - N2
147		L3 = I - N3
148		L4 = I - N4
149		L5 = I - N5
150	889	G(I) = Q1(I,L2)*X(I-2)+Q1(I,L3)*X(I-1) +Q1(I,L4)*X(I)+Q1(I,L5)*X(I+1)+Q1 (I,N3)*EXP(EK-EK/X(I)*X(L4)/(1.+DKV1* X(L4))

CARD NUMBER	STATEMENT NUMBER	STATEMENT
151		G(N1) = Q1(N1,N4-2)*X(N1-2)+Q1(N1, N4-1)*X(N1-1)+Q1(N1,N4)*X(N1)+Q1 (N1,N2)+Q1(N1,N3)*EXP(EK-EK/X(N1)) *X(N4)/(1,+DKV1*X(N4))
152	C	SUMMING ABSOLUTE VALUES
153		DIMENSION C4(50), R(N4), EFF(N4)
154		G1 = 0:0
155		DØ 600 I = 1, N1
156		G2 = ABS (G(I))
157	600	G1 = G2 + G1
158		C4(I1) = G1
159		I1 = I1 + 1
160	C	EVALUATING THE RIGHT HAND SIDE OF EQUATIONS
161		A(1,N8) = -G(1)+A(1,1)*X(1)+A(1,2)* X(2)+A(1,N2)*X(N2)+A(1,N3)*X(N3)
162		A(2,N8) = -G(2)+A(2,1)*X(1) +A(2,2)* X(2)+A(2,N2)*X(N2)+A(2,3)*X(3)+A(2, N3)*X(N3)+A(2,N2)*X(N2)
163		DØ 883 I = 3, N5
164		L2 = I + N9
165		L3 = I + N5
166		L4 = I + N4
167		L5 = I + N3
168	883	A(I,N8) = -G(I)+A(I,I-2)+X(I-2)+A (I,I-1)*X(I-1)+A(I,I+1)*X(I+1)+ A(I,I)*X(I)+A(I,L2)*X(L2)+A(I,L3) *X(L3)+A(I,L4)*X(L4)+A(I,L5)*X(L5)
169		A(N4,N8) = -G(N4)+A(N4,N9)*X(N9)+ A(N4,N5)*X(N5)+A(N4,N1-2)*X(N1-2) +A(N4,N1-1)*X(N1-1)+A(N4,N4)*X(N4) +A(N4,N1)*X(N1)
170		A(N3,N8) = -G(N3)+A(N3,1)*X(1)+A(N3,N3)*X(N3)+A(N3,N2)*X(N2)
171		A(N2,N8) = -G(N2)+A(N2,2)*X(2)+A (N2,N3)*X(N3)+A(N2,N2)*X(N2)+A (N2,N7)*X(N7)

CARD NUMBER	STATEMENT NUMBER	STATEMENT
172		DØ 767 I = N7, N6
173		L2 = I - N4
174	767	A(I,NØ) = -G(I)+A(I,L2)*X(L2)+ A(I,I-2)*X(I-2)+A(I,I-1)*X(I-1) +A(I,I)*X(I)+A(I,I+1)*X(I+1)
175		A(N1,N8) = -G(N1)+A(N1,N4)*X(N4) +A(N1,NN1)*X(NN1)+A(N1,N6)*X(N6) +A(N1,N1)*X(N1)
176	C	FINDING THE NEW IMPROVED ROOTS
177		N = N1
178	19	M = N+1
179		K1 = N
180	13	C = A(K1,K1)
181		DØ 9 I = 1, K1
182	9	A(K1,I) = A(K1,I)/C
183		A(K1,M) = A(K1,M/C
184		I = K1 - 1
185	11	D = A(I,K1)
186		DØ 10 J = 1, K1
187	10	A(I,J) = A(I,J) - D*A(K1,J)
188		A(I,M) = A(I,M) - D*A(K1,M)
189		I = I - 1
190		L = 0
191		IF(I.EQ.L) GØ TØ 12
192		GØ TØ 11
193	12	K1 = K1 - 1
194		L = 1
195		IF(K1.EQ.L) GØ TO 14
196		GØ TØ 13
197	14	E = A(K1, K1)
198		A(K1,M) = A(K1,M)/E
199		SUM = 0

CARD NUMBER	STATEMENT NUMBER	STATEMENT
200		DØ 16 I = 2, N
201		K1 = I - 1
202		DØ 15 J = 1, K1
203	15	SUM = SUM + A(I,J)*A(J,M)
204		A(I,M) = A(I,M) - SUM
205	16	SUM = 0
206		DØ 18 I = 1,N
207	18	X(I) = A(I,M)
208	C	EVALUATING THE RESIDUALS WITH NEW ROOTS
209		G(1)=Q1(1,1)*X(1)/X(N3)+Q1(1,2)*X(2) /X(N2)+Q1(1,N3)*EXP(EK-EK/X(N3))* X(1)/(1.+DKV1*X(1))
210		G(2)=Q1(2,1)*X(1)/X(N3)+Q1(2,2)*X(2)/ X(N2)+Q1(2,3)*X(3)/X(N7)+Q1(2,N3)* EXP(EK-EK/X(N2))*X(2)/(1.+DKV1*X(2))
211		DO 886 I=3,N5
212		L2=I+N9
213		L3=I+N5
214		L4=I+N4
215		L5=I+N3
216	886	G(I)=Q1(I,I-2)*X(I-2)/X(L2)+Q1(I,I-1) *X(I-1)/X(L3)+Q1(I,I)*X(I)/X(L4)+ Q1(I,I+1)*X(I+1)/X(L5)+Q1(I,N3)*EXP(EK-EK/X(L4))*X(I)/(1.+DKV1*X(I))
217		G(N4)=Q1(N4,N4-2)*X(N4-2)/X(N1-2)+Q1(N4,N4-1)*X(N4-1)/X(N1-1)+Q1(N4,N4)*X(N4) /X(N1)+Q1(N4,N2)+Q1(N4,N3)*EXP(EK-EK/ X(N4)/(1.+DKV1*X(N4))

CARD NUMBER	STATEMENT NUMBER	STATEMENT
218		G(N3)=Q1(N3,1)*X(N3)+Q1(N3,2)*X(N2) +Q1(N3,N3)*EXP(EK-EK/X(N3))*X(1)/ (1.+DKV1*X(1))
219		G(N2)=Q1(N2,1)*X(N3)+Q1(N2,2)*X(N2) +Q1(N2,3)*X(N7)+Q1(N2,N3)*EXP(EK-EK/ X(N2))*X(2)/(1.+DKV1*X(2))
220		DO 890 I=N7,N6
221		L2=I-N2
222		L3=I-N3
223		L4=I-N4
224		L5=I-N5
225	890	G(I)=Q1(I,L2)*X(I-2)+Q1(I,L3)*X(I-1)+ Q1(I,L4)*X(I)+Q1(I,L5)*X(I+1)+Q1(I,N3) *EXP(EK-EK/X(I))*X(L4)/(1.+DKV1*X(L4))
226		G(N1)=Q1(N1,N4-2)*X(N1-2)+Q1(N1,N4-1) *X(N1-1)+Q1(N1,N4)*X(N1)+Q1(N1,N2)+ Q1(N1,N3)*EXP(EK-EK/X(N1))*X(N4)/ (1.+DKV1*X(N4))
227	C	SUMMING THE NEW RESIDUALS
228		G1=0.0
229		DO 599 I=1,N1
230		G2=ABS(G(I))
231	599	G1=G2+G1
232		C4(I1)=G1
233	C	CHECKING FOR CONVERGENCE
234	C	COMPARING THE RESIDUALS SUM
235		IF(C4(I1).GE.C4(I1-1))GO TO 68

```
CARD NUMBER   STATEMENT NUMBER   STATEMENT
  236                           GO TO 67
  237             C             CALCULATE NEW INCREMENT IF NECESSARY
  238             68            I2=I2+1
  239                           I3=I3+1
  240                           IF(I3.LT.I2)GO TO 888
  241                           D1(I2)=D1(I2-1)/2
  242                           DO 171 I=1,N1
  243             171           X(I)=F(I)
  244                           GO TO 100
  245             888           I5=I5+1
  246                           B1=I5
  247                           D1(I2)=B+C6/B1
  248                           DO 175 I=1,N1
  249             175           X(I)=F(I)
  250                           GO TO 100
  251             67            V=.0005
  252             C             CHECKING THE SIZE OF EACH RESIDUAL
  253                           DO 555 I=1,N1
  254                           IF(ABS(G(I)).GT.V)GOTO 40
  255             555           CONTINUE
  256                           B=D1(I2)
  257                           I5=1
  258                           IF(D1(I2).GE.W)GO TO 150
  259                           CONTINUE
  260                           DO 173 I=1,N1
  261             173           F(I)=X(I)
  262                           I2=I2+1
  263                           D1(I2)=D1(I2-1)*2.
  264                           C6=ABS(D1(I2-2)-D1(I2-1))
  265                           GO TO 100
  266             150           CONTINUE
```

CARD NUMBER	STATEMENT NUMBER	STATEMENT
267		DO 176 I=1,N1
268	176	F(I)=X(I)
269	C	EVALUATION OF LOCAL EFFECTIVENESS FACTORS
270		RO=DKV*PX/(1.+DKV1*PX)
271		DO 73 I=1,N4
272		NN2=N3-1+I
273	73	R(I)=DKV*EXP(EK-EK/X(NN2))*X(I)/ (1.+DKV1*X(I))
274		DO 74 I=1,N4
275	74	EFF(I)=R(I)/RO
276	C	EVALUATION OF OVERALL EFFECTIVENESS FACTOR
277		DIMENSIONA3(5,6),A2(5,6),A1(5,6), Y1(5),Y2(5),Y3(5)
278		DO 800 J=1,6
279	800	A3(1,J)=1.000
280		DO 801 I=2,5
281	801	A3(I,1)=0.0000
282		DO 802 I=2,5
283	802	A3(I,2)=1./(4.**(I-1))
284		DO 803 I=2,5
285	803	A3(I,3)=1./(2.**(I-1))
286		DO 804 I=2,5
287	804	A3(I,4)=3.**(I-1)/(4.**(I-1))
288		DO 805 I=2,5
289	805	A3(I,5)=1.000
290		DO 806 I=2,5

CARD NUMBER	STATEMENT NUMBER	STATEMENT
291		B9=I
292	806	A3(I,6)=1./B9
293		DO 807 I=1,5
294		DO 807 J=1,6
295	807	A2(I,J)=A3(I,J)
296		DO 808 I=1,5
297		DO 808 J=1,6
298	808	A1(I,J)=A3(I,J)
299		DO 809 I=2,5
300	809	A2(I,2)=1./(7.**(I-1))
301		DO 810 I=2,5
302	810	A2(I,3)=3.**(I-1)/(7.**(I-1))
303		DO 811 I=2,5
304	811	A2(I,4)=5.**(I-1)/(7.**(I-1))
305		DO 812 I=2,5
306	812	A1(I,2)=2.**(I-1)/(7.**(I-1))
307		DO 813 I=2,5
308	813	A1(I,3)=4.**(I-1)/(7.**(I-1))
309		DO 814 I=2,5
310	814	A1(I,4)=6.**(I-1)/(7.**(I-1))
311	C	SOLVE THE MATRIX A3,A2,A1
312		DO 815 I=1,5
313		DO 815 J=1,6
314	815	A(I,J)=A3(I,J)
315		N=5
316		I10=2
317		I9=2
318		GO TO 19

CARD NUMBER	STATEMENT NUMBER	STATEMENT
319	816	CONTINUE
320		DO 817 I=1,5
321	817	Y3(I)=X(I)*7./DN1
322		DO 818 I=1,5
323		DO 818 J=1,6
324	818	A(I,J)=A2(I,J)
325		N=5
326		I10=3
327		I8=3
328		GO TO 19
329	819	CONTINUE
330		DO 820 I=1,5
331	820	Y2(I)=X(I)*8./DN1
332		DO 821 I=1,5
333		DO 821 J=1,6
334	821	A(I,J)=A1(I,J)
335		N=5
336		I10=4
337		I7=4
338		GO TO 19
339	822	CONTINUE
340		DO 823 I=1,5
341	823	Y1(I)=X(I)*7./DN1
342		DN10=0.0
343		I=2
344		J=1
345		K=1
346		GO TO 831

CARD NUMBER	STATEMENT NUMBER	STATEMENT
347	824	I=I+1
348		J=J+1
349		K=K+2
350	831	DN9=K
351		DN11=Y1(I)*EFF(J)*DN9**2
352		DN10=DN10+DN11
353		IF(I.EQ.4)GO TO 830
354		GO TO 824
355	830	DN12=0.00
356		B13=Y1(5)+Y2(1)
357		NN4=N4-7
358		NN5=N1-15
359		I=4
360		J=7
361		GO TO 832
362	825	I=I+4
363		J=J+8
364	832	DN9=J
365		DN13=B13*EFF(I)*DN9**2
366		DN12=DN13+DN12
367		DN25=N1-7
368		IF(I.EQ.NN4)GO TO 833
369	833	DN14=(Y2(5)+Y3(1))*EFF(NN4-3)*DN25**2
370		DN16=0.000
371		NN6=N4-6
372		NN7=N4-5
373		NN8=N4-4
374		NN9=N1-13
375		NN10=N1-12

CARD NUMBER	STATEMENT NUMBER	STATEMENT
376		NN11=N1-11
377		J=5
378		K=9
379		GO TO 834
380	826	J=J+4
381		K=K+8
382	834	DN9=K
383		DN15=Y2(2)*EFF(J)*DN9**2
384		DN16=DN15+DN16
385		IF(J.EQ.NN6)GO TO 835
386		GO TO 826
387	835	DN15=0.00
388		J=6
389		K=10
390		GO TO 836
391	827	J=J+4
392		K=K+8
393	836	DN9=K
394		DN17=Y2(3)*EFF(J)*DN9**2
395		IF(J.EQ.NN7)GO TO 837
396		GO TO 827
397	837	DN13=0.000
398		J=7
399		K=11
400		GO TO 838
401	828	J=J+4
402		K=K+4
403	838	DN9=K
404		DN18=Y2(4)*EFF(I)*DN9**2

CARD NUMBER	STATEMENT NUMBER	STATEMENT
405		DN13=DN13+DN18
406		IF(J.EQ.NN11)GO TO 839
407		GO TO 828
408		DN20=N1-5
409		DN21=N1-3
410		DN22=N1-1
411		DN19=Y3(2)*EFF(N9)*DN20**2+Y3(3)*EFF(N5)*DN21**2+Y3(4)*EFF(N4)*DN22**2+Y3(5)
412		EFFET=DN10+DN12+DN16+DN17+DN13+DN19
413		DN26=N1
414		EFF0=(3./DN26**2)*EFFET
415		THMOD=EFF0*DKV*RG*TS/(DEX*(1.+DKV1*PX))
416		BETA=CXS*DELH*DEX/(DALP*TS)
417		GAMMA=EK
418		CF=PX*DKV1
419	93	FORMAT(1X,21HGAMMA,BETA,TH.MOD.,CF)
420		WRITE(6,93)
421	2	FORMAT(1X,9F14.5)
422		WRITE(6,2)GAMMA,BETA,THMOD,CF
423	91	FORMAT(1X,27HLOCAL EFFECTIVENESS FACTORS)
424		WRITE(6,2)(EFF(I),I=1,N4)
425	105	FORMAT(1X,37HEFFECTIVENESS FACTOR AND, DEX,DALP,DKV)
426		WRITE(6,2)EFF0,DEX,DALP,DKV
427	6	FORMAT(1X,9HRESIDUALS)
428		WRITE(6,6)
429		WRITE(6,2)(G(I),I=1,N1)
430	7	FORMAT(1X,29HCONCENTRATION AND TEMPERATURE)
431		WRITE(6,7)
432		WRITE(6,2)(X(I),I=1,N1)

CARD NUMBER	STATEMENT NUMBER	STATEMENT
433	126	FORMAT(1X,50HSURFACE TEMP,PARTIAL PRESS ,HEAT OF REAX,DELTA R SQ)
434		WRITE(6,126)
435		WRITE(6,2)TS,PX,DELH,DELR
436		STOP
437		END

*** The following corrections are required to make the program work (Program 1).

Between card numbers 207 and 208

IF(I10.EQ.I9)GO TO 816

IF(I10.EQ.I8)GO TO 825

Between card numbers 368 and 369

GO TO 825

Program 2

CARD NUMBER	STATEMENT NUMBER	STATEMENT
24		P(1,1)=Z*(-1./DELR)
25		P(1,2)=-P(1,1)
26		P(2,1)=Z*DELR
27		P(2,2)=Z*(-2./DELR)
28		P(2,3)=Z*(1./DELR)
32		NO EQUIVALENT CARD...
33		P(I,I-1)=Z/DELR
34		P(I,I)=Z*(-2./DELR)
35		P(I,I+1)=Z/DELR
37		P(N4,N9)=Z*(-1./(5.*DELR))
38		P(N4,N5)=Z*(10./(5.*DELR))
39		P(N4,N4)=Z*(-25./(5.*DELR))
44		P(N4,N2)=Z*(16./(5.*DELR))*PX
45		P(N1,N2)=TS*DALP*(16./(5.*DELR))

** Cards 277 to 410 inclusive have no equivalent in Program 2

411		EFFET=0.000
412		DØ 75 I=1,N4
413	75	EFFET=EFF(I)+EFFET
414		EFF0=2/DN1*EFFET